# THE CYCLE OF WEATHERING

# THE CYCLE OF WEATHERING

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" mutat enim mundi naturam totius aetas
ex alioque alius status excipere omnia debet,
nec manet ulla sui similis res: omnia migrant,
omnia commutat natura et vertere cogit.
namque aliut putrescit et aevo debile languet,
porro aliut clarescit et e contemptibus exit.
sic igitur mundi naturam totius aetas
mutat et ex alio terram status excipit alter,
quod pote uti nequeat, possit quod non tulit ante."

*T. Lucreti Cari : De rerum Natura*
*(lib. V., 828-836)*

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## AUTHOR'S PREFACE.

THIS book was published in Russian towards the end of 1934, and in issuing it I did not expect much success. Nevertheless it was quickly sold out and is now difficult to obtain.[1]

The theory of types of crust of weathering that I have advanced has been widely adopted in my country, not only by my own pupils. I therefore felt that an English edition might serve a useful purpose.

That the laborious work of translation should be undertaken by my friend and pupil, Dr. Alexander Muir, has given me great pleasure.

B. B. POLYNOV.

Moscow.

*December 14th*, 1936.

[1] The Russian edition comprised 3,000 copies.—(Translator.)

# FOREWORD

## BY W. G. OGG, M.A., PH.D.

MOST of the earlier investigations of soils had a utilitarian object in view, viz., to increase their productivity. This farmyard outlook was understandable and has achieved a great deal in the way of developing our knowledge of systems of manuring and general soil treatment for higher crop production. Many of the methods of treatment, however, are still somewhat empirical owing to a lack of knowledge of the soil.

The scientific study of the soil itself was first developed by the Russians, and their early work on morphology, classification and distribution has done much to stimulate soil research in other countries. The laboratory studies, however, have not kept pace with the field side of soil work, although there have been notable advances in certain directions such as adsorption and base exchange. This weakness on the laboratory side of pedology has led to considerable confusion in soil classification and survey work, and has also handicapped the investigation of fertility problems.

The soil is the living outer shell of the crust of weathering of the earth, and pedology might well have developed as a branch of geology. Unfortunately geologists have paid rather scant attention to the crust of weathering and particularly little to the outer sheath in which the biologist and the farmer are also interested.

In other words the study of the fundamental raw material of the soil has been neglected, and because of this the new science of pedology has been handicapped from the start.

Fortunately this is now being remedied, and Professor Polynov's admirable study of *The Cycle of Weathering* is

a most valuable contribution to our knowledge of the subject. Scattered data existed in many geological and other text books, but in this work Professor Polynov has brought these together and has added the results of his own extensive researches. He has traced the cycles of the various elements in the crust of weathering and has developed a philosophy of the weathering processes which will undoubtedly prove a great stimulation to soil research. It is likely to provide the basis for a more satisfactory system of soil classification and to put soil investigations on a more satisfactory scientific basis.

Professor Polynov is particularly well qualified to deal with the subject, for he is eminent not only as a pedologist but also as a mineralogist. He has been fortunate in his translator, Dr. Muir, who studied in Russia for two years and has taken a special interest in this branch of soil work.

This part of Professor Polynov's work deals with the cycle of weathering and with the weathering processes. His second volume will deal particularly with soils. Together they will prove most valuable not only to soil workers but to geologists and geographers.

## TRANSLATOR'S NOTE

In making this translation I have followed the original as closely as possible. Any alteration and revision has been sanctioned by the author, who has co-operated wholeheartedly with me throughout, and to whom I express my thanks. I alone am responsible for the Appendix. It is hoped that the index which has been added to this edition will prove serviceable. My colleague, Dr. R. L. Mitchell, has been kind enough to read both manuscript and proofs; Professor E. F. Bailey, now Director of the Geological Survey, read the proofs and checked the geological terminology, saving me from several misstatements, and Dr. A. Brammall kindly allowed me to read an unpublished manuscript on the clay minerals. The encouragement and help of my chief, Dr. Ogg, has lightened considerably the task of translation. To all these gentlemen I wish to express my gratitude for their assistance.

ALEX. MUIR.

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CHAPTER I

# THE EARTH'S CRUST AND THE CRUST OF WEATHERING

## 1. The Conception of the Earth's Crust

Even a superficial acquaintance with the stages in the history of our conception of the earth itself, its crust, the rocks composing it, and the minerals making up the rocks, discloses the fact that one of the most important factors in the development of our ideas is the conflict between two sets of quite different theories. On the one hand we have the ideas of rest, equilibrium and inertia, and on the other those of continuity, movement and change. It appears that the progressive epochs in that history are connected with the prevalence of the second group of ideas. It thus becomes clear that in our epoch, the epoch of the greatest advances in science, current philosophy has arrived at a conception of the universe as a continuous everlasting process.

We ought really to say has again arrived, for the idea is not new in the history of science. In the fifth century B.C. Heracleitus expressed in his famous statement *παντα ῥεῖ* (everything flows) the conclusions of a fairly well developed conception of the world. This doubtless had its roots in the past and certainly had a definite influence on the development of ancient philosophy. And however deep appears to be the difference, at first sight, between the present day cosmogenic and geological outlook, and the teachings of the " obscure " philosopher,[1] there is between them an evolutionary connection such as in general exists between ancient and modern philosophy. But this evolution was not direct, logically consecutive and uninterrupted. It was

[1] Heracleitus, insufficiently understood by his contemporaries, was given the sobriquet *σχοτεινος* (obscure). In England he is generally called the " weeping " philosopher.

carried along as on a wave, and epochs in which it prevailed alternated with periods when it was lost sight of. One of the epochs in which the idea was uppermost produced that genial poem of Lucretius, *De Rerum Natura* (first century B.C.), in which we find a purely materialistic (atomic) conception of the world of Democritus and Epicurus with a striking combination of the ideas of movement and change.

This idea exerted a strong influence during the following centuries and is found not only among the alchemists of the Græco-Egyptian period (VI century), but even after sixteen centuries it occurs in the views of the famous naturalist, Georg Bauer (Agricola) and with still greater clarity in the teachings of Giordano Bruno.

During the Middle Ages scientific thought was in decadence; religious influence was strong, and the effect was to produce the conception of the creation of the earth as of a completed act, and as a necessary corollary the ideas of rest and equilibrium. These and other ideas had a very great influence and have penetrated almost to the present day. The lapidary (a list of minerals) of the Middle Ages preordained the descriptive character of mineralogy, and focussed attention on the outward form, colour, taste and other directly perceptible properties of minerals. These properties were valued as constants that determined some or other variety of a mineral and soon gave rise to the idea of minerals as constant and unalterable individuals. That these could undergo fundamental changes never found a place in the philosophical theories of the period.

The XV century and later saw development of the idea of the everlasting process, and elements of it are found in the writings of Leonardo da Vinci (XV-XVI century) and Stenon (XVII century). It appears in the polemics of the " neptunist " school of Werner and the " vulcanists " led by Hutton at the beginning of the XVIII century. But the birth of the idea in its most general form is to be found in Lyell's famous *Principles of Geology* (1830-1833).

This is already the XIX century, towards the end of which the ground is being prepared for the teachings of geological cycles, for the recognition of the processes of

metamorphism and the deciphering of the mysterious "petrographical hieroglyphics"—the "mute" crystalline schists; for the development of mineralogy as a genetic science and not simply a descriptive one. The subdivision of the earth's crust into thermodynamic shells was to come, and preparation made for the development of two new geological disciplines—soil science in the XIX and geochemistry in the XX century. These have as the objects of their study not stable but continuously changing forms, and if we are allowed to speak of equilibrium between these, then it is only as a somewhat abstract moment in a continuous process.

In this way the starting point of the modern concept of the world and the universe was formed. One of the most fundamental and essential problems connected with this concept is, of course, the problem of the structure of matter. The atom, sometime fundamental brick of the universe, has been found to be a complex dynamic system which is capable of disintegration and internal change. Its place is now taken by the electron as the elementary unit, and the knowledge of the properties of the latter, breaking down the boundary between matter and energy, leads us more and more to a solution of the problem of the single substance on the basis of which is built the vast number of physico-chemical phenomena.

Having as our object an exposition of the earth's crust we cannot widen our theme with a survey and analysis of the modern physico-chemical conception of matter. And although sooner or later the solution of problems of this type is bound to be reflected in the geological sciences, we are forced at present to start from the coarser and less profound, but nevertheless true, conception of solid matter as a varied collection of atoms of the different elements. We will also be compelled to contrast energy and mass (weighable material) without doubting, however, the unity of matter and energy. This contrast of matter and energy is used to distinguish various different phenomena that have one and the same origin. Perhaps the time has come for the introduction of a new terminology which would save us the neces-

sity of such explanations and our treatment from apparent dualism, but for the present we must carry on without it.

Let us now return to the modern concepts of the earth and of the earth's crust.

The inner part of our planet—the barysphere, is wrapped round by a solid sheath—the lithosphere, which in its turn is covered incompletely by a water sheath, the hydrosphere, and above that by the complete covering of the atmosphere. The barysphere is, so far, a region beyond the reach of our investigations, and we have no clear ideas of the condition in which matter exists there, but with a fair degree of truth we may say that matter in the barysphere must have a high specific gravity. Finally, although geology in the accurate sense of the word—the science of the earth—ought to study the whole earth, it actually confines itself to the investigation of the earth's crust and gives little attention to problems of the state and composition of the barysphere.[1]

The earth's crust is the whole thickness of the outer sheaths: the lithosphere, the hydrosphere and the atmosphere. The lithosphere is not uniform throughout, but the matter composing it varies in its form and in the grouping of its atoms and compounds with the variations of temperature and pressure. In this connexion three thermodynamic belts are recognized within the lithosphere—the lower, lying at a depth greater than 16-20 km.—the magmatic region, where pressure has a hydrostatic character and exceeds 5,000 atmospheres, whilst the temperature reaches something like 1000°; above that stretches the zone of metamorphism with a unilateral pressure measured in thousands of atmospheres and a temperature fluctuating fairly widely above and below the critical temperature of water (374°); and, finally, the uppermost belt, or zone, of weathering with a temperature like that of the earth's surface and a pressure varying from one atmosphere to that found at the bottom of oceans. The relative content of silica decreases from the magmatic belt outwards, whilst those of oxygen and water increase. The sharp contrast between the compositions of the lithosphere, hydrosphere and atmosphere is obvious. The depth

[1] This is the problem of geophysics.

of the water sheath, we know, varies greatly; its greatest value approaches 10 km. and its mean is about 3,700 m. There are some difficulties in the measurement of the atmospheric sheath, for with increasing altitude gas rarification prevents the formation of a definite boundary such as the upper boundaries of the lithosphere and hydrosphere provide. Within the atmospheric zone, however, separate belts can be recognized: the troposphere or nitrogen-oxygen zone, which reaches approximately 15 km. above sea level, and above that the stratosphere, the region of rarefied gases, in the upper part of which we may assume the disruption of molecules and the stability of free atoms. The upper boundary of the atmosphere has been variously determined, and the greatest value given reaches 4,800 geographical miles (Laplace).[1]

## 2. Cyclic Processes in the Earth's Crust

The static model of the structure of the earth which we have just outlined obviously requires substantial correction: it is not difficult to see the unreality of such a model. Indeed, one doubts whether it is possible to assume such a tranquil state of equilibrium in a system of contiguous masses of material having very different temperatures and different arrangements of elements and compounds. No profound analysis of the physical and chemical properties of that system is necessary to show that it is not in equilibrium; and, in fact, from the study of the earth's crust we may look on its condition not as in static equilibrium but as a stage in a process of which certain moments are fixed by our minds. This study shows us that the earth's crust is by no means in a state of rest but is undergoing complex changes that are brought about on the one hand by the intermingling of masses within the crust itself, and on the other by the deformations and transformations resulting from that inter-

[1] Other determinations give figures of another order: 60-80 km. (diffraction of sunlight by particles in the air), 150 km. (observations on falling stars which flame up on entering the atmosphere), 300-500 km. (observations on the aurora borealis). If we take into consideration the fact that above a certain limit the particles in the air are not affected by gravity and scatter out into space, then, strictly speaking, no upper limit for the atmosphere can exist.

mingling. The mixing of masses may take place either in a horizontal or vertical direction. Centuries of fluctuations in the earth's crust, local earthquakes, mountain building processes, volcanic activity, disintegrating actions of surface ice, water and air, have all helped to change its structure and its surface features. The outlines of the continents and of the seas are altered: what was once the bottom of the sea has been raised up to the height of the everlasting snows, whilst high mountains have been worn down, levelled and buried under the sea. The material forming the lithosphere here undergoes shrinkage, rupture and fracture, and elsewhere consolidation, recrystallization and like changes.

In all these movements and changes may be seen a certain " cyclic " succession. Volcanic processes bring up to the surface of the lithosphere, or into the zone of weathering, viscous magmatic material, impregnated with gases and vapours. The gases and vapours escape into the atmosphere or hydrosphere, and on the surface of the lithosphere the lavas cool and solidify to form the so-called extrusive igneous rocks. If the magma does not reach the surface, but cools at some depth, it gives rise to plutonic igneous rocks. In course of time both the extrusive and plutonic rocks are broken down under the action of the sun's rays and atmospheric agents, and the debris from their disintegration is carried, mechanically or in solution, to the oceanic basins and there laid down to form stratified sedimentary rocks. Becoming more and more deeply buried under new deposits, the layers of earlier deposits are consolidated and cemented. Falling into the zone of metamorphism on the lowering of the earth's crust, these sedimentary rocks, under the influence of high temperature and pressure, are deformed still more. The compounds present crystallize, and in this way are formed the so-called crystalline schists—rocks characteristic of the zone of metamorphism. Under the influence of lateral pressure, sedimentary and metamorphic rocks crumple up and form various folds, faults, thrusts, etc. The pressures giving rise to these deformations may at the same time bring about still further metamorphism of the rocks.

Igneous rocks also may undergo changes in structure and texture if they fall into the zone of metamorphism. Their granular crystalline texture, in which the individual grains, crystals, are variously oriented and distributed, under the influence of a unilateral pressure, is changed so that the crystals become reoriented and redistributed in a definite way, depending on the pressure. For example, in granites all the plates of mica are reorientated so that they lie parallel to each other, forming gneisses. In this way igneous and sedimentary rocks are metamorphosed. On further submergence they may reach the magmatic belt, become molten, and so give rise to new material which can again be brought up to the surface of the lithosphere as igneous rock.

We thus see that in the earth's crust there take place diverse transformations of material which form, as it were, an unending cycle—a cyclic process, in which after a series of changes matter invariably returns to its original form. Such cycles may be followed not only for the great mass of rock-forming material, but also for many individual substances. Thus, sulphur passes through various states characteristic of the different sheaths and zones of the earth's crust, from the albumens of organisms through sulphates, dissolved in sea water and scattered through the air as a fine dust, to the metallic sulphides of the plutonic rocks thrown up from the magmatic zone. The sulphides are transformed by the weathering of these rocks into sulphates and albumens, and so sulphur undergoes its cycle of weathering, embracing the whole of the earth's crust. Included in these large cycles may be smaller ones which do not extend outside one belt or zone. The same sulphur, without leaving the zone of weathering, can be taken up by plants in the form of sulphates, converted into albuminous matter, and returned again after the death and decomposition of the plant in the form of sulphate. In this case the sulphur completes a small cycle.

From this it follows that the compounds of some elements change their form according to the thermodynamic medium in which they occur. Compounds formed in the deeper zones of the earth's crust have been given the name *juvenile*, whilst the forms which they assume in the belt of

weathering and in the upper sheaths are called *vadose*.[1] In many cases the compound is the same whether it occurs in juvenile or vadose forms: thus we distinguish juvenile and vadose water, carbon dioxide and silica.

The similarity in chemical composition of several juvenile and vadose forms is explained by their great stability, which allows them to exist under widely different thermodynamic conditions (*e.g.* free silica). The similarity in chemical composition, however, does not mean that their state of aggregation is the same; it is different for the different zones. Finally, time is a factor in all processes, and therefore it occasionally happens that the juvenile and vadose forms are not quite typical of their sheaths, but represent transition, sometimes very temporary, stages in the change to the more stable form for the given conditions. It is important that this last circumstance be carefully taken into consideration. Dealing as we are with a continuous process, we cannot expect that in each zone, in each sheath of the earth's crust, at any given moment, the compounds and forms present will be in full equilibrium with the thermodynamic medium. That would mean a return to the static model which we have already rejected. But since cyclic processes such as we have described do occur, it is evident that at any given moment we may observe compounds in various stages of transformation, each moving towards a form and status corresponding to the given zone. The state finally reached is only stable so long as the compounds remain in that zone: the moment they leave it and enter new thermodynamic conditions they will necessarily undergo new transformations. It is in this way that the transformation of matter in the earth's crust takes place.

If we assume that the cyclic process which embraces all the matter of the earth's crust is *fully reversible*, we arrive at an unreal model, the invalidity of which is shown by theoretical considerations and undoubted facts.

[1] V. I. Vernadsky distinguishes another group, *phreatic* compounds, which are characteristic of the zone of metamorphism. It is not always possible, however, to differentiate phreatic compounds from those of juvenile origin. We therefore will not use this distinction, and have occasionally used the term "primary" compounds to include both juvenile and phreatic compounds found in the crust of weathering.

Consideration of the following points will make this obvious:—

(a) If the cyclic process consisted merely in the complete transfer of a mass of material from one sheath to another, changing only the form and grouping of the atoms within that mass, then the ultimate chemical composition of all the sheaths would be the same. Since that is not the case, we may assume that during the cycle there takes place a certain redistribution of the elements and their compounds in the sheaths, *i.e.* some elements are predominantly held in one sheath, whilst others are held in another sheath. If, therefore, preferential accumulation takes place there is not complete reversibility in the cyclic process.

(b) The cyclic process in one way or another embraces the hydrosphere and atmosphere. In these occurs the dissemination of the juvenile gases and vapours; the oxygen of the atmosphere oxidizes many juvenile and vadose compounds; the water of the sea dissolves and hydrates the sediments, and so on. At the same time these sheaths have a chemical composition contrasting sharply with that of the lithosphere. One consists almost exclusively of an oxide of hydrogen, while the other consists to a large extent of nitrogen. Such a condition may be explained either as the result of a process of transformation and redistribution of material, or because these sheaths have always existed independently of the process of transformation of matter in the lithosphere, in which they take part only to a small extent at the present time. We shall accept the first proposition and disprove the second later; *i.e.* we shall again acknowledge that the cycle of matter is not a fully reversible process, that it does not bring all matter completely back to its original state, but has a somewhat definite progressive movement which leads to a redistribution of elements and states.

(c) A comparison of the present-day state of the earth with the conditions on other planets and heavenly bodies, some having hydrogen-helium atmospheres with metallic gases and clouds, others almost devoid of any atmosphere whatever, convinces us that the earth with its liquid water sheath and its nitrogen-oxygen atmosphere is simply at one

stage in the transformation of heavenly bodies. We thus arrive at the conclusion that the structural model of the earth and the earth's crust, which is fixed by our senses, shows that the earth has had another state in the past and that it will assume a new one in the future.

If we regard the cycle of the vadose sulphur compounds as a small part of a larger sulphur cycle in the earth's crust, then we must consider the latter and the cyclic processes going on in it to be parts only of a still greater cycle—the transformation of the matter of the earth and of the universe.

But it is incorrect to express the cyclic processes of the earth's crust as closed circles. These "cyclic" processes have at the same time a progressive movement, and would be more correctly expressed as a curve traced by a point on

FIG. 1.—Complex Cycloid.

the circumference of a circle rolling in a straight line. Such a curve is known as a cycloid.[1] A complex cycloid may be taken as the symbol for the cyclic processes of the whole earth's crust, with little constituent cycles representing transformations restricted to individual sheaths or their parts (*Fig.* 1).

The subject of our study is not the whole earth's crust, but that part only which bears the name crust or zone of weathering. In considering that alone we limit ourselves more or less artificially; we separate from the whole process certain parts of it—from the unbroken curve of the complex cycloid we select only a small piece. But the study of the nature of that piece by itself is possible only provided its place on the general curve is recognized. That condition does not allow us to leave out of consideration entirely other parts of the earth's crust. We shall have to consider especially

[1] Prof. Dr. Link, Die Kreislaufvorgange im Mineralreich, Jena, 1912.

frequently the sheaths that cover the lithosphere, these being very closely connected with the phenomena and transformations on its surface.

We shall now focus our attention on the crust of weathering.

### 3. Formation of the Crust of Weathering

The words stone and rock have long been used by many peoples to signify durability and stability, but this is not borne out by a closer observation of nature. Peoples dwelling in mountainous regions know the instability of rocks and cliffs, as is indeed shown by the Finnish name for the coarse-grained granite peculiar to that country. It is known as rappakivi,—literally, rotten rock. According to the famous geologist Heim, the people in certain parts of Switzerland say of a weak-minded and morally unreliable person that he is as undependable as a cliff. And this is said by people who spend their lives among rocky mountains and observe the disintegration with their own eyes.

Each massive solid rock appearing in the outer sheath of the lithosphere inevitably undergoes disintegration, and sooner or later assumes the form of a loose, or clastic, deposit. The immediate cause of this disintegration is in most cases temperature fluctuation, which is the more effective the nearer the rock is to the surface. Raindrops falling on flint which has been warmed by the sun's rays can produce cracks in it. Still more quickly disintegrated are those complex rocks consisting of a variety of minerals each with a different coefficient of expansion. Water and solutions filling the cracks in cliffs and rocks thrust the sides apart when they freeze, and thus assist still more in the disintegration, which is completed by the dynamic action of moving ice, water and wind. It is evident that such effects cannot be observed in the part of the lithosphere surface now covered with water—the bottoms of seas and oceans. In these the process of *deposition* of sediments predominates, and pressure and temperature are more constant. But we must not forget that the configuration of the oceans and continents during the existence of our planet has been greatly

changed and is even now changing, and where there is now sea there may have been, and may yet be, dry land. Looking at this process of disintegration on a historico-geological scale, we must recognize it as the greatest factor in the transformation of matter and quite characteristic of the surface part of the lithosphere.

The change of rocks from the massive to the clastic state, or, as it is called, the *weathering*[1] of massive rocks, is not confined solely to a change in their outward form, but brings with it a whole series of processes resulting in the transference and transformation of matter. The breaking down of a massive monolith of rock, or, in general, solid body, results in an increase in the surface area of that body, *i.e.* the interface between it and the surrounding medium. But we know that every interface, *e.g.* the boundary between solid and liquid, or solid and gaseous states, possesses quite specific physico-dynamic properties, which become more important both quantitatively and qualitatively as the ratio of the interface to the surrounding mass, *i.e.* the specific surface, increases. The enormous rate of growth of the total and specific surface as a solid body is ground down is common knowledge. It is sufficient to remember that if we break up a cube of 1 cm. side (6 sq. cm. surface, and volume 1 c.c.) into particles having each a side of 0·01 mm., the total surface of the fine material reaches 6,000 sq. cm., and in the same way the specific surface of each particle increases in comparison with the specific surface of the original cubic centimetre. The enormous molecular forces contained in the solid body neutralize each other before it is broken up, but afterwards these can interact with the surrounding medium, and, naturally, the greater the surface in contact with the medium the more rapid will be the interaction. A large number of examples of such surface reactions are known. Among them

[1] By this term most authors understand the disintegration and transformation of minerals or rocks which takes place under the influence of the sun, atmospheric agents, organisms, and solutions formed by the circulation of rain water in the upper sheath of the lithosphere. A. Penk limits the process of weathering to those effects of the agents mentioned which take place *in situ*, and do not include the transference of material. The majority of workers, however, do not accept this limited interpretation, and include in the term weathering nearly all the processes of denudation.

we have the surface adsorption of gases and vapours, but the most important point in the transformation of matter is when solid bodies, having attained a certain specific surface, yet remaining in the solid state, become able to take part through their surfaces in reactions with dissociated ions in solution, in other words, take part in reactions of a chemical nature.[1] On the other hand, the dispersion and solution of solid bodies are connected with the increase in specific surface. However great be the specific gravity of any solid body, *e.g.* iron or copper, a piece of it can be ground up into such a fine powder that it will not sink in water. In such a powder the ratio of the surface of the individual particles to their mass reaches such a magnitude that the combination of surface forces occurring between the particle and the surrounding water so exceeds its mass (force of gravity) that the particle either remains suspended in the water or sinks at such an infinitely slow rate that it cannot be observed.

The dispersion of solid matter may take place in a gaseous as well as in a liquid medium. Since the interaction between the surface of the dispersed solid particles and the liquid increases as the particle becomes smaller, it is not surprising that the state of dispersion gradually passes into dissociation, *i.e.* the breaking up of the molecules into ions, or chemical solution. All this makes it clear that under similar conditions any clastic rock is more reactive than the same amount of similar material in the form of a solid mass or compact lumps.

*The disintegration and comminution of massive rocks is in this way a change of matter into a more active state. In this process the forms of matter are altered and the transformation is brought about both by cosmic, especially solar, energy absorbed by the rock and by the internal energy inherent in matter in the solid state set free on the breaking up of the rock.* This process being extremely important and characteristic of the upper part of the lithosphere, naturally

[1] This refutes the former view held until nearly the middle of the XIX century. This stated that chemical interaction is only possible between liquid bodies (corpora non agunt, nisi fluida).

differentiates that sheath from the rest. That sheath we shall call the *crust of weathering*.

*Thus, the crust of weathering is that upper part of the lithosphere which consists of the loose products of the disintegration of igneous and metamorphic rocks.*

Comparing the compactness of these igneous and metamorphic rocks with the loose state of the crust of weathering, the fluid state of the hydrosphere and the gaseous state of the atmosphere, we become convinced that matter as it moves from the depths of the earth's crust to its periphery tends to assume a more and more scattered or *disperse* state. And it may be said that the difference between the sheaths consists chiefly in the degree of dispersion of the material. The quantitative character of this difference becomes especially clear if we take into consideration the fact that the minerals of igneous and metamorphic rocks contain scattered bubbles of liquids, gases and vapours, that water solutions, vapours and gases circulate among the solid particles of the loose crust of weathering, while the atmosphere and hydrosphere are by nature disperse systems. Each of these sheaths represents a peculiar complex disperse system, and they differ one from the other not only in the degree of dispersion but in the nature of the dispersion medium and the dispersed phase that it contains.

In the deeper parts of the lithosphere the dispersion medium is a solid mass, and the dispersed phase consists of scattered inclusions of liquids and gases; the hydrosphere has as its dispersion medium liquid water which contains dissolved gases and solids; the atmosphere is a gaseous medium with scattered vapours and solids. In these sheaths the boundaries between the dispersion medium and the dispersed phase are clear and definite. The crust of weathering, on the other hand, is characterized by the *indefiniteness* of these boundaries, and within it the change from the dispersion medium into the dispersed phase is usual within quite short distances. Thus in sand with a porosity of 30-40% the dispersion medium is without doubt the solid mass, but in deposits in which the porosity reaches 60% and more, the solid mass changes into the dispersed phase, and the water

or air occluded in the pores may be considered as the dispersion medium.

## 4. Fundamental Processes in the Crust of Weathering

All the properties and peculiarities of the crust of weathering are, as we have seen, the result of its loose, finely divided state. But however important or characteristic this state may be for the crust of weathering, neither it nor its consequences are sufficient for the complete or even the general characterization of that sheath. In order to complete the characterization it is necessary to consider certain other phenomena.

Let us suppose that we are in a region of volcanic activity, *e.g.* in the neighbourhood of Vesuvius, and are observing the action of solfataras,—the evolution of *juvenile* sulphur in the vapour state. These vapours, practically before our eyes, change first into the liquid, and then into the solid state. It is evident that this process takes place with the *loss of heat.* Solid sulphur on the surface of the earth is not a completely stable system: sooner or later, either by direct chemical reaction or with the help of micro-organisms, it is oxidized, and this oxidation is exothermic, *i.e.* it takes place with evolution of heat. The reaction may be represented by the scheme:—

$$S+3O=SO_3+102{,}160 \text{ calories},^1$$

*i.e.* the combination of 32·06 g. sulphur with 48 g. oxygen forms 80·06 g. sulphuric anhydride with the evolution of 102,160 cals. of heat energy. The oxide formed is, however, quite unstable, and avidly combines with water to form sulphuric acid. This is also very reactive, and forms sulphates on interaction with various salts and their bases. These reactions also take place with the evolution of heat.

[1] Thermodynamic equations, such as those given, illustrate the well-known law: the sum of energy and matter is a constant quantity. This law, however, contradicts the law of Lavoisier. Actually we may say that the masses on either side of the equation are equal, with the proviso that the mass of 102,160 cals. is minute and incommensurable in comparison with the masses of S, O and $SO_3$. In this way the mass equation: $S+3O=SO_3$ may be considered correct. Actually the mass corresponding to 102,160 calories is equal to $48.10^{-9}$g.

$$SO_3 + H_2O = H_2SO_4 + 20{,}470 \text{ cals.}$$

$$H_2SO_4 + K_2CO_3 = K_2SO_4 + H_2O + CO_2 + 195{,}500 \text{ cals.}$$

The sulphates are more stable but they, too, strive to assume still more stable forms—the least soluble salts, in this case calcium sulphate:—

$$K_2SO_4 + CaCl_2 = CaSO_4 + 2KCl + 13{,}570 \text{ cals.}$$

In this way we see that juvenile sulphur on reaching the earth's surface undergoes a series of transformations under the influence of the oxygen and water in the air, and is altered not only in state of aggregation, but also in its combination with other elements. All these transformations which take place with the evolution of heat bring S into the most stable and most inert state under the given conditions.

Sulphur lying on the surface of the earth in a medium containing oxygen and vaporous or liquid water is like a stone hanging on the edge of a cliff: it contains a certain store of potential energy. And when the stone breaks off and falls to the bottom it arrives at a state of rest: so, in a similar way, sulphur dissipates energy during its transformations before finally passing into its most inert compounds. We have reason to believe that the example given characterizes, in general, that series of transformations which is undergone by a material of juvenile origin when it reaches the earth's surface or the crust of weathering. As a result of these exothermic transformations the heat energy evolved will in part, enter the outer sheaths,—the hydrosphere and the atmosphere, and partly be scattered into space, the crust of weathering accumulating the most inert and least mobile forms of matter. This is confirmed to some extent by the widespread distribution on the earth's surface, and within the crust of weathering, of oxides, water, carbonates and other salt-forming compounds, which, being the results of interaction of the elements of the lithosphere with oxygen, water and carbon dioxide of the atmosphere, are actually very inactive compounds and, if capable of taking part in a reaction, do so, for the most part, only if there is an inflow of energy.

These compounds become buried during succeeding ages in the layers of sedimentary rocks in the deeper shells of the earth's crust and there change their forms and the grouping of the elements: new stores of energy are gained, and when the substances return to the surface the energy is again dissipated in the reactions in the crust of weathering.

It thus appears that the breaking up of rocks brings them into a more active state, and that the series of exothermic reactions in which juvenile substances appearing in the crust of weathering take part, are directed towards the evolution of energy, which, becoming kinetic in the crust of weathering, is finally scattered into space.

It would, however, be a great mistake to characterize the crust of weathering simply as the region of dissipation of energy and the formation of inert compounds. In that case it would simply become a storehouse of useless immobile material.

Actually it is in that same crust of weathering, as we shall show later, that diametrically opposed processes take place in great numbers and diversity: processes of absorption and accumulation of energy: the formation of active *endothermic* compounds and systems.

Anyone who has travelled by boat from the town of Sterensk down the Shilka will no doubt remember the so-called "Tsagan smoking mountains." These are first of all not mountains but the high, steep precipice of the left bank of the Shilka, which consists at that point of a great depth of sand and sandstone beds. In the daytime the upper part of a certain strip of that bank emits wreaths of smoke that is especially abundant and dense after rain, when it rolls down to the river and wraps round the ship, making breathing difficult for the passengers on deck. During the night, instead of smoke, fantastic moving lights are interspersed from time to time with "smoke snakes" that run down the bank to the river.

For some time this phenomena proved an enigma, and it was even suggested that it was due to volcanic action. It was later found that in these Tsagan sands are layers of lignite. The sands are gradually worn away and the lignite

becomes ignited when only a thin covering of loose sand is left. This at once explains the appearance of the smoke. It is evident that here the burning (oxidation) takes place at the expense of thermal energy, but the energy used up is not the *juvenile energy of matter coming from the depths of the earth's crust but cosmic energy* previously absorbed and accumulated by a special form of matter—living matter.

The necessary condition of life, and of the development of green plants is not only a definite amount of heat, but also of light: solar heat and light. These forms of cosmic radiant energy that our planet receives are absorbed by green plants and are used in the conversion of the carbon dioxide, water and mineral elements of the soil taken up by the plant into new compounds rich in energy (endothermic): starch, glutens, sugars, albumen, etc. Green plants give these compounds to other vegetable organisms (parasites, saprophytes) and to herbivorous animals, the latter passing them on to carnivorous animals. The innumerable putrifying and fermenting micro-organisms feed on the synthesized products, too, and in this way cosmic energy is distributed over our planet in a special medium—living matter.

The reproduction and spreading of organisms becomes in consequence a factor in the increase and distribution of cosmic energy on the earth. With the diverse transformations that living matter brings about and the various organic compounds which it generates, this energy assumes different forms: kinetic, thermal, chemical, etc., and involves, as we shall see later, the interaction of the various elements of the lithosphere, hydrosphere and atmosphere. Lignite, rich in carbon, the product of the transformation of vegetable remains, is only one of the various forms of accumulation of cosmic energy. Its combustion, like the breathing of living organisms, and the putrefaction of their dead bodies and residues, takes place with the evolution of heat, and consequently with a certain dissipation of energy. We must not forget the myriads of minute organisms inhabiting land and water, which invariably absorb cosmic energy and use it in the processes taking place on the earth.

The domain of "living matter" is called the *biosphere*.[1] This includes the whole of the hydrosphere[2], the lower parts of the atmosphere and the upper sheath of the lithosphere. This part of the lithosphere, included in the biosphere, extends to the depth to which roots and micro-organisms occur; and it is evidently a part of the crust of weathering. The crust of weathering does not, therefore, coincide completely with the biosphere, but that part of it which is included in the biosphere is marked by all the processes peculiar to living matter. Here take place the propagation and development of organisms, and the greater proportion of these spend all stages of their development in the crust of weathering, working out special forms suitable for existence in the earth (*e.g.* earth-worms, lower fungi and soil micro-organisms). In the crust of weathering takes place also the decomposition of their dead bodies and organic residues. Other transformations lead to the accumulation of carbon in the form of lignite, anthracite, coal, schungite; hydrocarbons in the form of petroleum, osokerite, bituminous shales, and other deposits. It is necessary to note that these have left the limits of the active biosphere and are the means by which accumulations of cosmic energy penetrate into the lower parts of the crust of weathering and then into the deeper sheaths of the earth's crust.

In this way we see that in the crust of weathering there takes place an accumulation of energy as well as its dissipation and scattering; that is endothermic reactions in addition to exothermic. These endothermic reactions are not confined to the synthesis of organic compounds into living matter, but, as we shall see shortly, appear in many processes, involving mineral compounds. Thus, reversing as it were, the oxidation of juvenile sulphur compounds

[1] The first to consider the biosphere as a special sheath of the earth's crust was E. Suess (1875). Nevertheless, the geological rôle of the biosphere and of living matter in the earth's crust was only recently elucidated in the excellent work of V. I. Vernadsky. This work in Russian and French only began to appear in 1922. The most complete exposition of his views is to be found in his books, "The Biosphere" (Leningrad, 1926) and "Geochemistry" (Leningrad, 1927). There are French and German versions of the latter.

[2] It used to be thought that life could not exist below 600-1,000 m., but the *Challenger* expedition, towards the end of the XIX century, showed that life could exist even at the greatest depths.

($FeS_2$,$H_2S$) there take place in the crust of weathering, under the influence of the decomposition of organic remains, certain reduction processes, and to some extent sulphuric change into the more active sulphurous compounds, and even into free sulphur. Similarly, in contrast to the ordinary processes of hydration and carbonate formation, which take place during weathering, we have the processes of dehydration and the setting free of the carbon dioxide of carbonates. And even the inert nitrogen of the air, with the assistance of micro-organisms, passes through a whole series of compounds, accompanied by fairly energetic reactions.

## 5. General Characteristics of the Zone and the Crust of Weathering

Let us now summarize all that we have said so far about the crust and zone of weathering. The crust of weathering is the upper part of the lithosphere, in which any solid massive material that enters from deeper zones of the earth's crust is changed into a loose clastic state and increases its surface of contact with the gaseous, vaporous and liquid phases of the outer sheaths of the earth's crust. This process takes time, and at the present moment it is obvious that in different places the crust of weathering has arrived at different stages in its development. In many cases bare granite, gneiss or other igneous or metamorphic rock outcrops on the surface of the lithosphere. This means that the outcropping rock has not yet had time to be transformed into a clastic state, but the process of disintegration is indubitably taking place already. Actually, if we investigate carefully the bare parts of such rocks we will always find some indication or other of the beginnings of disintegration : cracks, the accumulation of large blocks at the foot of cliffs, screes, rubble and gravel, and, in a greater or less amount, still finer material such as sand or clay.

It follows then that we ought to distinguish the following : (1) *The region or zone of weathering, i.e.,* that upper part of the lithosphere which in different places and at different times may consist of various materials such as igneous and metamorphic masses, and loose sedimentary rocks, *but*

*within which the processes are directed towards the disintegration and comminution of rocks and the formation of the crust of weathering;* (2) *the present-day crust of weathering, i.e.* those parts of the surface sheath of the lithosphere which at this moment already consist of loose, disintegrated products of weathering; in other words, of any kind of sediment or deposit, and sedimentary rocks not yet undergoing metamorphism.

The thickness of the zone or region of weathering is determined by the depth to which the agents of weathering penetrate, *i.e.* fluctuations in temperature and the action of solutions, oxygen, carbon dioxide of the air, and other vadose agents. This depth is reckoned at about 0·5 km. from the surface of the lithosphere, *i.e.* from the surface of dry land or the bottoms of seas and oceans. To a more accurate determination of this depth we shall return later. As regards the thickness of the present-day crust of weathering, it cannot exceed that of the zone of weathering, but it may be as little as 1 m. or less. The thinnest parts occur on outcrops of igneous intrusions or metamorphic rocks or recently cooled lavas. When the crust of weathering is formed it is not entirely uniform; we can distinguish an upper, fairly distinct part occupied by the biosphere, *i.e.* the soil.

The whole crust of weathering consists, in general, of a complex disperse system in which the solid phase occupies about 70% of the whole, the rest consisting of gaseous and liquid phases. The components of these phases interact, and the large interface between them increases the amount and intensity of such reactions. The energy of reaction and movement in the zone and crust of weathering has two different sources: (1) The deeper zones of the lithosphere from which comes material with a store of energy, which is transformed in the zone of weathering into various active forms; (2) radiant cosmic, and especially solar energy, which is absorbed by the upper sheaths of the earth's crust, including the zone of weathering, and similarly undergoes transformation.[1] An especially great but not exclusive part in this transformation

[1] V. I. Vernadsky distinguishes three sources of the energy of geological processes: (1) cosmic (including solar), (2) earth's, and (3) internal energy of matter (*vide* "Geochemistry").

is played by the biosphere, and consequently by the soil, in the crust of weathering.

Corresponding to the absorption and dissipation of energy occurring in the zone of weathering, all the processes taking place in it may be divided into two categories: those which involve evolution of energy—exothermic, and those which involve absorption of energy—endothermic. To the first category belong the processes which lower the dispersion of the material, for example, the change from the gaseous to the liquid and from the liquid to the solid state; the absorption of gases by liquids and solids, reactions of hydration and oxidation, including the respiration of organisms and the decomposition of their remains, a whole series of subsequent reactions leading to the formation of least soluble neutral salts, etc.

All these processes result in the formation of the most inactive forms of matter, which, however, do not build up a store of inert material, but may again take part in reactions during the processes of the second category. These bring about an increase in the degree of dispersion of material systems (*i.e.* the disintegration of solid bodies, change of the same to liquid and gaseous states) increase in the reactivity of solutions and gases on increase in temperature, processes of reduction, and the synthesis of organic compounds in the metabolism and reproduction of organisms.

These exo- and endothermic reactions are closely interrelated and give rise to those partial cycles and to those parts of the general cycle of the transformation of matter which are peculiar to the crust of weathering.

We shall examine these cycles in more detail in the following chapters.

## CHAPTER II

# THE OXYGEN, CARBON AND NITROGEN CYCLES IN THE CRUST OF WEATHERING

### 1. Distribution of the Elements in the Earth's Crust and in the Crust of Weathering

The questions that we shall consider in this and the following chapters may be stated in the following way: in what compounds does any element enter the zone of weathering, what changes do these compounds undergo in this zone, and in what form do they leave it? For a complete elucidation of these problems we, unfortunately, do not have the necessary material at present. The fate of many elements, not only in the crust of weathering but also in the whole earth's crust, is still vague and obscure. Even if we focus our attention on the commoner elements we are often unable to follow the forms and stages in the transformation of their compounds.

Up to the present we can recognize about 90 elements which go to make up the earth. This number, of course, is not final, and we have reason to believe that it may be increased.[1] We know that the amounts of the different elements in the earth's crust differ greatly.[2] The first place is occupied by Oxygen which makes up about half (49·3%) of the mass of the whole earth's crust; the second place is held by Silicon with 25·67%. Next we have a group of six elements whose percentage contents do not exceed 10% and are not less than 1%. In decreasing order this group consists of: Aluminium (7·5%), Iron (4·7%), Calcium (3·39%), Sodium (2·63%), Potassium (2·40%), and Magnesium

[1] It is possible that in the earth there are little known elements which have so far been observed only in certain stars by spectrum analysis.

[2] The average chemical composition of the earth's crust was arrived at by recalculating the content of each element given in the analysis of river, lake and sea water, igneous, metamorphic and sedimentary rocks, on the basis of the area occupied by these.

(1·93%). The third group of elements have contents ranging between 1% and 0·1% and likewise contains six members: HYDROGEN (0·87%), TITANIUM (0·58%), CHLORINE (0·19%), CARBON (0·10%), MANGANESE (0·10%) and PHOSPHORUS (0·10%). The fourth and final group consists of five elements: SULPHUR (0·06%), BARIUM (0·04%), NITROGEN (0·03%), FLUORINE (0·03%) and STRONTIUM (0·02%). It is obvious that the remaining elements, including any as yet unknown, do not account for more than 0·5% of the whole mass of the earth's crust.

A somewhat different picture is obtained if we compare the volumes (more accurately the number of atoms) of these elements. In this case we get the following series: OXYGEN (53·8%), HYDROGEN (17·18%), SILICON (16.85%), ALUMINIUM (4·76%), SODIUM (1·80%), MAGNESIUM (1·67%), CALCIUM (1·44%), IRON (1·30%), POTASSIUM (1·04%), CARBON (0·58%), TITANIUM (0·18%), CHLORINE (0·10%), PHOSPHORUS (0·05%), SULPHUR (0·05%) and MANGANESE (0·03%).

Thus from these approximate figures we obtain some idea of the contemporary (in the widest geological sense) composition of the earth's crust. As we have already mentioned, the composition of the crust of weathering ought to differ to some extent from the composition of the whole earth's crust.[1] Certain differences may be observed *a priori*.

There can be no doubt that the contents of oxygen, hydrogen and chlorine in the crust of weathering increase on account of the close contact of the latter with the hydrosphere and the atmosphere. The amount of carbon increases due to its partial association with the biosphere, which is rich in carbon, and it is likely that nitrogen is also present to a greater extent. It is obvious that a relative increase in the contents of these elements ought to be reflected in the decrease in the contents of the others, and of these iron and magnesium apparently decrease most markedly. Accumulations of these two elements are characteristic of the deeper zones of the earth's crust.[2] If we assume that the relative amount of an

[1] We cannot assess the average composition of the crust of weathering from the analysis of sedimentary rocks, drifts and soils, since these analyses do not take into account the elements of soil air which make up about 30% of the volume of clastic rocks.

[2] Ferro-magnesian compounds of the earth's crust are predominantly concentrated in the deep basic magmas of a basaltic type.

element by mass or volume in any shell more or less determines its part in the transformations and movements of material within this shell, then the first place must be given to oxygen. We shall therefore begin this survey with the compounds of oxygen.

## 2. Juvenile Carbon Dioxide and Its Transformations: the Formation of Free Oxygen. The Fundamental Biological Cycle of Oxygen

The juvenile forms in which oxygen enters the zone of weathering, the hydrosphere and the atmosphere must be looked for in the gaseous, vaporous and liquid volcanic and post-volcanic eruptions, lavas and plutonic igneous rocks. It should be mentioned first of all that oxygen is present in combination with other elements in all the substances which find their way into the zone of weathering. Up to the present there is no authoritative record of free juvenile oxygen, and there is reason to believe that this form, $O_2$, is characteristic exclusively of the upper shells of the earth's crust.[1]

The juvenile compounds of oxygen may be divided into four main groups: (1) Carbon dioxide of volcanic and post-volcanic eruptions; (2) water of similar origin; (3) oxides of metals and metalloids in the form of the solid minerals of igneous rocks; and (4) salt-like compounds also in the form of minerals in igneous rocks.

The presence of juvenile carbonic acid and oxides of carbon in gaseous volcanic discharges is well known. In some cases it has been found that carbonic acid represents about 90% of all the gaseous products (Santorin). We also know that the most intense evolution of $CO_2$ takes place neither during the greatest activity, nor at the main crater where the other gases and vapours are given off, but at points some distance from the centre and in the later and quieter stages of the activity. To this type are assigned the so-called mofettes (carbonic acid fumaroles), and especially evolutions of carbon dioxide in the regions of ancient (tertiary) volcanic

[1] Even if we assume that a certain amount of $O_2$ is of juvenile origin, its amount is immeasurably smaller than that of vadose oxygen formed in the biosphere.

activity. The famous " Grotto del Cane " is an example of this type, and has appeared in many text-books of geography. These descriptions often make the evolution of $CO_2$ by the earth seem like a miracle occurring only in this one place, whereas it is only a single case of an extremely common process. This process, although occurring at the present day, is actually a very protracted one, occupying millions of years, and it may be observed in many parts of the continents of Eurasia and America. The Phlegrean Fields in Italy, Auvergne in France, and the Northern Caucasus, by no means exhaust the number of localities in Europe where juvenile $CO_2$ is evolved. It is probably given off as free gas or as gas saturating mineral springs in many places as yet unknown.[1]

The juvenile $CO_2$ given off in this way mixes with the atmosphere, is absorbed by the water of the hydrosphere, and circulated with the air and solutions in the crust and zone of weathering. It thus becomes an important factor in organic life and in the decomposition of rocks and minerals. This double rôle of $CO_2$ in the zone of weathering corresponds to the two categories of important processes in the oxygen cycle: (1) Plant metabolism and (2) the formation of salts of carbonic acid.

The most important stage in plant metabolism is the synthesis of organic compounds of the carbohydrate group (starch), a process whose mechanism is hidden in the chlorophyll cells of the organism. It is in these cells, with the aid of the sun's energy, that the synthesis of the carbon dioxide from the air and water taken up by the roots from the soil into complex compounds takes place.[2] The organic compounds formed in this way undergo further changes in the plant organism and provide a basis for the formation of all the other organic compounds (other carbohydrates, fats, pro-

[1] Thus, for example, emanations of $CO_2$ were discovered during the excavations of the Alkhan-Churtov canal in the N. Caucasus in 1929.

[2] It is now known, nevertheless, that certain organisms, devoid of chlorophyll (*e.g.* nitrifying bacteria) have the power of assimilating $CO_2$. In this case the splitting up of $CO_2$ is done by the chemical energy of oxidation reactions. Such a process, therefore, is called chemical synthesis, in contradistinction to photosynthesis (light synthesis). In the general processes of the carbon and oxygen cycles chemical synthesis plays a subordinate part in comparison with photosynthesis.

teins, etc.) that are necessary for the building up of the plant's tissues and organs. If we remember that all other organisms (animals, saprophytes and parasites of vegetable origin) use the organic matter of plants as the source of their food, it is clear that carbon dioxide is the primary source of all the organic compounds of living matter.

At present, however we are concerned with the fate of oxygen and not of carbon, and we are only interested in $CO_2$ as an oxygen compound. From that point of view, we must remember that in the same chlorophyll cells there takes place a breaking down of $CO_2$, and, at the same time as carbon enters into the composition of the organic compounds of the plant organism, oxygen is set free and is given off by the plant in the free state, *i.e.*

$$\text{absorbed } CO_2 = C \text{ of organic compounds} + O_2.$$

This extremely important fact leads us to the conclusion that the free oxygen of the atmosphere has as its sole source the $CO_2$ absorbed by green plants from the air. No other way in which it could be formed is known.

The amount of free oxygen in the atmosphere has been calculated by Arrhenius at 1,216 billion metric tons. V. I. Vernadsky states that the amount of all the free oxygen, *i.e.* not only that in the atmosphere, but also the free oxygen in the hydrosphere and in the zone of weathering, is a little over 1,500 billion metric tons. This is about 1/10,000 of all the oxygen in the earth's crust. In any case the relative content of free oxygen in the earth's atmosphere is somewhat greater than that in the atmosphere of the sun, and we can thus say that certain phases in the existence of the earth are characterized by the *accumulation* in its atmosphere of free oxygen.

Free oxygen under the conditions of the earth's surface is chemically stable in a medium of free nitrogen and the inert gases.[1] In the biosphere and crust of weathering, however, that same oxygen is no less reactive than $CO_2$, and in the same way takes an active part in the life of organisms and the decomposition of rocks. As a result of the action

[1] Neon, argon, krypton, xenon, helium.

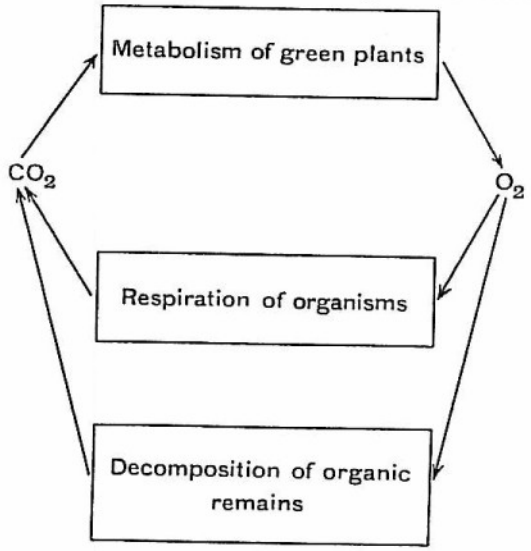
of oxygen, oxides of the metals and metalloids are formed. Of all these oxides, vadose $CO_2$ is of especially great importance. Even if we assume the possibility of the purely chemical formation of vadose $CO_2$ (*e.g.* the oxidation of juvenile lower oxides of carbon, there is no doubt that in the great majority of cases it is a result of biological processes. To this group first of all belong: the *oxygen respiration of organisms,* the *decomposition* (oxidation) of their remains, and their *putrefaction.* In respiration, the combustion of the carbon of organic compounds and the formation of $CO_2$ is carried out by myriads of cells in the individual plants and animals peopling land, sea and air. The decomposition of organic remains can, in certain cases, be assumed to be a direct oxidation by the oxygen of the air, but in the main this process is carried out by the activity of various micro-organisms. Even the process of spontaneous combustion of organic remains is begun by thermogenic bacteria, although it is later carried on by purely chemical reactions.

The microbiological process of *putrefaction* of organic remains gives rise to products of incomplete oxidation, *i.e.,* hydrocarbons and carbon monoxide. These products, however, are unstable and ephemeral in the crust of weathering. They are rapidly oxidized, and this process, as we shall see later, is also of a microbiological nature. If putrefaction, in this way, does not by itself give rise to $CO_2$, it at least prepares the carbon compounds for easy and rapid oxidation. For the carbon of organic compounds to escape this oxidation it must quickly leave the biosphere, as happens in the case of coal formation.

We see that this is a widely diffused process that is directly opposed to the formation of free oxygen. The $CO_2$ that provided a source of free oxygen by its decomposition in the organs of green plants is now reformed from carbon and oxygen, again through the agency of organisms. This time, however, not only green plants but also animals and organic remains in general take a direct part in the reaction. This process may be expressed by the equation:—

$$O_2 + C \text{ (of organic compounds)} = CO_2.$$

It is not difficult to reach the conclusion that these two contrasted processes are necessary parts of a greater and more complex transformation of organic compounds—a transformation that is the basis of life, and embraces the most active forms of oxygen compounds in the earth's crust. It may be expressed diagrammatically as follows:—




It is self-evident that the vadose $CO_2$ can take part in that cycle as well as the juvenile form. This cyclic process, apparently, occurs throughout the whole biosphere. It takes place in the waters of the ocean, where among the *plankton*, *i.e.* passively floating organisms, we find an infinite number that contain chlorophyll, some unicellular and some more complexly organized absorbers of energy. The cycle also proceeds to a greater or less extent in the atmosphere. In the crust of weathering it is found, strictly speaking, only in the uppermost part—the soil. But since the immediate factors and products of this cycle, oxygen and carbon dioxide, are to be found even in the deeper parts of the crust of weathering, and since the extensive part of the surface of the crust occupied by green plants participates directly in the production and circulation of oxygen and $CO_2$,

it is evident that this oxygen cycle and the crust of weathering are closely interdependent. We obtain a much better idea of the importance of this fact if we bear in mind that the content of $CO_2$ in the so-called soil air, *i.e.* in the air which circulates between the particles of loose surface deposits rich in organic remains, sometimes reaches 10%, whereas in the atmosphere it fluctuates within narrow limits around 0·05%. So, in the crust of weathering, clothed in its green mantle of energy absorbers, where every instant sees the birth and death of an infinite number of organisms, the processes in the oxygen cycle attain their fullest development.

### 3. Carbonates

The scheme which we have just outlined for the oxygen cycle, if accepted without reservations, might be taken as the expression of a closed equilibrium system in which all magnitudes can be given a definite numerical value. Actually, as we have already seen, such a conception would be untrue. We know that the appearance, not only of green plants, but also of organisms in general, is connected with a definite stage in the history of the earth, and consequently this form of oxygen cycle has in the same way its own beginnings and its quantitative development. It is obvious, of course, that this system cannot be a closed one; for one thing, juvenile $CO_2$ enters it from without, and a certain amount of the $CO_2$ and free oxygen leave it on being used up in the formation of carbonates and in the oxidation of other elements and compounds apart from carbon. We shall now take up these interactions which were not considered in the above scheme; interactions in which both $CO_2$ and oxygen take part. We have already seen that juvenile $CO_2$ can take part in the formation of carbonates, but it is obvious that since the process occurs in the upper shells of the earth's crust, vadose $CO_2$ may also take part.

All cases of the formation of carbonates in the zone of weathering and in the hydrosphere may be divided into two general groups: (1) The formation of carbonates by the direct action of $CO_2$ on the elements of rocks and minerals, and (2) processes of *organization* of carbonates.

Processes of the first kind may be expressed in a comparatively simple form :—

$$\underset{\text{silicate.}}{RSiO_3} + CO_2 + H_2O = \underset{\text{carbonate.}}{RCO_3} + SiO_2 + H_2O.$$

This means that $CO_2$ dissolved in the waters circulating in the crust of weathering or directly adsorbed on the surface of rocks or minerals, interacts with these and from silicates, aluminosilicates, and other salt-like compounds, forms carbonates in accordance with the above scheme. These carbonates, of course, can also interact with other salts, *e.g.*:—

$$Na_2CO_3 + CaCl_2 = CaCO_3 + 2NaCl,$$

and so exchange their bases. It is natural, therefore, that in the zone and crust of weathering we find vadose carbonates of various bases, thus, $Na_2CO_3$, $MgCO_3$, $CaCO_3$, $FeCO_3$, $MnCO_3$, $BaCO_3$, $SrCO_3$, $CuCO_3$ and others.[1] The distribution of these, however, is not uniform; some are unstable on account of their easy solubility, $Na_2CO_3$ for example, and form accumulations only in rare cases where conditions are especially favourable (*e.g.* soda lakes); others, which are compounds of lower oxides ($FeCO_3$), can only exist for any time under conditions where there is little oxygen; the members of the third group are not common because they are compounds of comparatively rare bases ($BaCO_3$, $SrCO_3$); and, finally, the most widespread are those minerals which consist largely of calcium carbonate (calcite, aragonite, lublinite), magnesium carbonate (magnesite) and the double salt, $CaMg(CO_3)_2$ (dolomite). In addition to these forms which have a quite definite chemical composition and structure, a large number of other formations are known, in which $CaCO_3$ plays a principal part, but so far their detailed chemical composition and state of aggregation is unknown. Thus, in every soil in areas of arid continental climate both in temperate and tropical regions, provided it was not formed from a rock absolutely devoid of Ca compounds (*e.g.* quartz sands or quartzite), we invariably encounter such formations. They appear in the form either of various kinds of concre-

[1] It must be noted that juvenile and phreatic carbonates also exist.

tions or earthy masses of varying compactness, or crusts or films covering pieces of rock or gravel, or finally they may be uniformly distributed throughout the loose material and not visible to the naked eye. They may be encountered in a greater variety of forms than seems to be realized by mineralogists who have paid and continue to pay scant attention to such formations, characteristic as they are for drifts and soils. Even in the most complete treatises on mineralogy we find neither descriptions of these forms nor information on their composition or genesis. The absence of anything about them in treatises, however, does not prevent them existing in nature and being obvious at every step. They permeate the deep loess deposits of the Siberian and Middle Asiatic steppes and deserts and also those around the Black Sea; they completely cover the loams of the Middle and Lower Volga and the loose sandy loamy crust of weathering of the Gobi plateau; they fill the Caspian deposits, the ancient and contemporaneous alluvium of the steppe rivers, and their widespread distribution in certain other parts of the world may be foretold. These carbonates are typical products of subaerial weathering.

To another category belong the processes of *organization* of carbonates and especially of *calcium carbonate, i.e.* processes that result in carbonate becoming the material for the building up of some parts or other of an organism. A comparison of the composition of the mineral matter dissolved in river water and the composition of the salts of sea water shows a decided difference. In particular, a sharp drop in the contents of calcium and combined $CO_2$ (*i.e.* of carbonates) is always observed. The differences in the composition of the salts dissolved in the large rivers of the Atlantic basin and the water of the ocean itself can be seen from the following table:—

| | Ca. | $CO_3$. |
|---|---|---|
| Rhine ... ... | 26·5% | 46·9% |
| Hudson ... ... | 20·7% | 35·4% |
| Mississippi ... ... | 22·9% | 51·6% |
| Atlantic Ocean ... | 1·2-1·4% | 0·2-0·3% |

Data for other rivers of the Atlantic Basin could be quoted,

but since the figures are all of the same magnitude as those given, there is no need to present them. The fall in the content of Ca and combined $CO_2$ in the salts of sea water can be considered a fully established fact.

We thus see that very large amounts of calcium and carbonate ions dissolved in river water are removed from solution when they enter sea water. Their removal is brought about by an infinite number of marine organisms which use the $CaCO_3$ extracted from solution to build up their shells, inner skeletons and other parts. To this great group of organisms which "organize" and accumulate $CaCO_3$ belong the unicellular aquatic plankton, whole classes of the simplest organisms such as foraminifera and radiolaria, certain sponges, cœlenterata, and particularly various corals, which build up reefs and islands, needle-fish (sea urchins, sea lilies, starfish and others), brachiopods, molluscs, and even certain worms (annelids). After the death of these organisms, their hard calcareous skeletal parts are deposited on the sea bottom to form great depths of sediments, measurable in hundreds of metres, and containing a certain amount of $CaCO_3$. These more or less calcareous silts formed the beginnings of the numerous sedimentary calcareous rocks (marl, chalk, shelly and other limestones).

The processes just described are typical of the hydrosphere and aqueous parts of the crust of weathering. Individual examples of the organization of $CaCO_3$ are also known on dry land: for example, in the shells of land snails, the calcareous skins of certain fruits, etc. There are also many other, more or less transitional, forms of $CaCO_3$ accumulation, *e.g.* the formation of shell marl in lakes, accumulations of lime on the leaves of the aquatic *Potamogeton*, the formation of limy tubes around the roots of plants. These are doubtless brought about by the action of the organisms, but in themselves they are not parts of these organisms. It is also probable that there is a certain amount of interchange between subaerial and marine carbonate formations. The $CaCO_3$ dissolved from loess and similar continental deposits, on entering marine basins undergoes *organization*, and the $CaCO_3$ of marl, chalk, and limestone, after these

have been disintegrated on the earth's surface, is carried in solution, or even mechanically, into the region of clastic deposits, and may once again give rise to various $CaCO_3$ accumulations. The change of the shells of molluscs into an earthy mass of $CaCO_3$ has been followed by the author in the Don valley.

The formation of limestones is a very important phase in the circulation of oxygen in the zone of weathering. Important in the first place because up to the present time immense amounts of $CO_2$ (and consequently of $O_2$) have been accumulated in this form, and, secondly, because this is the form in which $CO_2$ leaves the crust of weathering and enters the zone of metamorphism or still deeper regions. We thus have here a stage in the greater oxygen cycle.

As regards the amount of $CO_2$ bound up at the present time in limestones, it has been calculated to be 31,000 billion metric tons. According to Högbom and Chamberlain it is about 25,000 times greater than the amount of $CO_2$ in the air; other calculations make it 13,000 times greater.[1]

A certain compensation for this loss of free $O_2$ from the zone and crust of weathering is found in decarbonization, in which carbonates give up their $CO_2$. Such reactions are known in the zone of weathering. A good example is the reaction between carbonates and the sulphuric acid formed by the oxidation of juvenile and vadose sulphur, $H_2S$, or certain sulphides:—

$$SO_3 + RCO_3 + H_2O = RSO_4 + CO_2 + H_2O.$$

Reversible reactions of the following type are also known:—

$$R_2CO_3 + SiO_2 + H_2O \rightleftharpoons R_2SiO_3 + CO_2 + H_2O,$$

and we can assume that within the crust of weathering there are occasionally conditions which are favourable to this reaction proceeding from left to right.

To this type belong those cases of the adsorption by so-called "acid" soils of the metallic radicles of carbonates present in solution. In the proper place we shall discuss more fully these "acid" soils and explain the above and analogous adsorption reactions.

[1] S. Arrhenius, Das Werden der Welten (1907).

How far the processes of *decarbonization* compensate for the loss of $CO_2$ from the crust of weathering in the form of carbonates we are not in a position to state, but it is necessary to bear in mind that limestone is a form in which combined $CO_2$ frequently remains for a long time in the crust of weathering. The dissolution of this rock on land and its subsequent reformation on the sea bottom also constitutes a small cycle which recurs in the crust of weathering in the course of millions of years.

### 4. Microbiological Processes of Oxidation and Their Products. Direct Oxidation

Oxidation (*i.e.* combination with oxygen) is undergone not only by carbon, but also by a large number of compounds and other native elements. In the group of elements we have: hydrogen, sulphur, nitrogen, phosphorus, iron, manganese, copper, lead, zinc, mercury and other less common metals and metalloids. Among the oxidation processes characteristic of the crust of weathering the complex microbiological reactions must be accorded a special place on account of their importance. The classical example is *nitrification*. The nitrogen of the air exists in constant contact with oxygen and yet does not interact with it to form compounds if we except the small amount of oxides formed during atmospheric electrical discharges. On the other hand, the nitrogen of organic compounds, when these undergo decomposition, is converted into ammoniacal salts which are oxidized to salts of nitrous acid. These last on further oxidation give salts of nitric acid.[1] These reactions may be represented by the equations:—

(1) $2NH_3 + 3O_2 = 2HNO_2 + 2H_2O$.

(2) $2HNO_2 + O_2 = 2HNO_3$.

The first stage is brought about by specific bacteria of the type *Nitrosomonas, Nitrosococcus,* and the second by another kind of bacteria, *Nitrobacter*. These oxidation processes provide the source of energy which the micro-organism re-

[1] On the entrance of nitrogen into the composition of organic compounds, *v. infra,* p. 63.

quire in order to assimilate free $CO_2$; in other words, this is their peculiar method of breathing.[1]

It is important to note here that these processes are the origin of the formation in the crust of weathering of the natural compounds of oxygen with nitrogen, including those nitrates and nitrites which occur in the most diverse soils in small quantities, and those rich deposits of soda saltpetre in Chili and Peru, the potash saltpetre in India (Bengal saltpetre), Algeria and other less important localities. Everywhere the oxidation of inert nitrogen is carried out at the expense of the energy of living matter—of nitrifying micro-organisms.

Analogous to what we have just described is the microbiological oxidation of sulphur. This is undergone by juvenile and vadose sulphur as well as the sulphur of sulphides, for example, iron sulphide in the form of pyrites or in the colloidal state—hydrotroilite ($FeS.H_2O$), which is typical of medicinal mineral muds. If we start with a vadose compound of sulphur, say $H_2S$, we can distinguish two stages in the oxidation :—

(1) $2H_2S + O_2 = 2H_2O + S_2$.

(2) $S_2 + 2H_2O + 3O_2 = 2H_2SO_4$.

The first consists in the oxidation of hydrogen and the separation of sulphur which precipitates in the form of drops in the protoplasm of sulphur bacteria (*Beggiatoa, Thioploca, Thiothrix, Chromatium, Rabdochromatium, Amœbobacter,* and others); the second in the oxidation of that sulphur; a process again playing a part in the respiration of the organisms. The sulphuric acid formed in this way and the nitric acid formed in nitrification at once interact with every kind of compound containing bases, whether carbonates or silicates, and give rise to sulphates and nitrates of the metals. Such compounds ($H_2SO_4$, $HNO_3$) may exist in the free state in the crust of weathering only for a very short time. Under special conditions, however, when they do not encounter sufficient bases for the formation of salts, they may have a

[1] Recent work has shown the possibility of the oxidation of ammonia to nitrous acid without micro-organisms. (See Rao and Dhar, *Soil Science,* 1931, **31**, 379-384.)

longer existence, and natural occurrences of free sulphuric acid are actually known. These are apparently the result of the microbiological oxidation of sulphur and the subsequent accumulation of the acid.[1]

The oxidation of hydrogen and of methane, which are always present in the atmosphere[2] and to a greater extent in the soil air, is also carried out by micro-organisms (*Bacterium pantatrophus, B. methanica, B. pyrocyaneum*). It appears that owing to this oxidation neither new volcanic emanations of hydrogen or hydrocarbons, nor the natural processes of hydrogen and methane fermentation which accompany the decomposition of organic compounds, increase to any extent the content of hydrogen or hydrocarbons in the air. It is specially important to note that these processes take place in the soil.

We have reason to believe that the oxidation of the phosphorus of organic compounds during their decomposition is likewise a microbiological process. As a result of this oxidation and the subsequent reaction of the phosphoric acid with the other compounds in the crust of weathering, there are formed a series of vadose phosphates. Among these are vivianite ($Fe_3(PO_4)_2.8H_2O$), which is found in bogs and swamps, phosphates characteristic of guano deposits, brushite ($HCaPO_4.2H_2O$), newberyite ($HMgPO_4.3H_2O$), and of sewers, struvite ($NH_4MgPO_4.6H_2O$), and many others.

Finally, it has been definitely established that the oxidation of natural compounds of ferrous iron, as well as of oxides of manganese, takes place in the crust of weathering through the medium of micro-organisms (*Leptothrix ochracea, L. crassa, Crenothrix polyspora, Galionella ferruginea,* and other iron bacteria). This process also plays a part in the part of respiration of the iron bacteria and takes place according to the equation :—

$$2FeCO_3 + 3H_2O + O = 2Fe(OH)_3 + 2CO_2.$$

Bogs, ponds, lakes and iron springs are places where such

[1] This occurs in the deserts of Kara-Kum in Middle Asia, *cf.* A. Fersman *et al.* "Sulphur" (a symposium), Leningrad, 1926, *Academy of Sciences.*

[2] According to Gautier 100 l. of atmospheric air contain about 20 cc. $H_2$.

processes occur with particular intensity and where, as a result, accumulations of iron-manganese hydrated oxides are found in the form of so-called bog iron ore, etc.

Nevertheless, by no means all oxidation processes that occur in the crust of weathering are of a microbiological nature. A number of widely distributed cases of the formation of oxygen compounds are, apparently, the result of direct interaction between oxygen and various kinds of minerals. To this type belongs, first of all, the weathering of silicates of iron and manganese. These silicates are the common salts of ferrous-iron and divalent manganese in isomorphous mixture with silicates of Mg, Ca, etc. Their decomposition on weathering can be represented by the following equations in which one of the stages is the formation of a carbonate:—

(1) $RSiO_3 + H_2O + CO_2 = RCO_3 + SiO_2 + H_2O$.

(2) $2RCO_3 + O + H_2O = R_2O_3.H_2O + 2CO_2$.

The formation in this way of the hydrated oxides of iron and manganese ($Mn_2O_3.H_2O$), the latter being further oxidized to $MnO_2$, is a common process, although the products for the most part do not form any accumulations, but are mixed with the weathering products of aluminosilicate and silicate rocks. A much higher content of manganese in the earthy products of weathering is found where primary silicates especially rich in manganese (*e.g.* rhodonite, $MnSiO_3$) undergo weathering.

There also takes place in the zone of weathering, independently of microbiological processes, the oxidation of native iron and copper. The second of these gives rise to cuprite, a new vadose mineral:—

$$2Cu + O = Cu_2O.$$

Oxidation of this kind is undergone by many vadose minerals also, and in this case often takes several stages. An excellent example of such changes is found in the oxidation of vivianite. We have just given this mineral as an example of the formation of a vadose phosphate. While it remains vadose, however, it undergoes further oxidation, passing finally into a ferric-iron phosphate, beraunite, of the com-

position $3Fe_2O_3.2P_2O_5.17H_2O$. The formation of vivianite, a ferrous salt, is due in the first place to microbiological action in some way or other, or connected with the decomposition of organic residues, but the further changes into beraunite through a series of intermediate ferro-ferric forms ($\alpha$-kerchenite, $\beta$-kerchenite, oxy-kerchenite) take place outside the influence of micro-organisms, and in all the stages in the transformation, from the first to the last, the crystalline structure of the mineral is retained. Without a doubt, the transformation of vivianite in the crust of weathering is only one of the innumerable cases of oxidation characteristic of that shell. While microbiological and biological oxidation is concentrated chiefly in the soil layer, that is, in the zone where there is a partial intermingling of the biosphere with the crust of weathering, the phenomena of direct oxidation occur throughout the whole zone of weathering and confer on it and the compounds present their peculiar character.

Processes of direct oxidation, nevertheless, are not confined solely to the zone of weathering, but occur in all the upper shells, including the hydrosphere and the atmosphere. Characteristic of the latter are such high degrees of oxidation as are found in the hydrogen peroxide and ozone which result from electrical discharges, the action of sunlight and ultraviolet radiation. It is also probable that these oxidations take place extensively in atmospheric dust which is ever present in the air in small quantities. We must take these processes into consideration, since when their products fall into the zone of weathering they become part of it and may finish the work of oxidation which is characteristic of this shell. Ozone and hydrogen peroxide ought to play such a rôle. It should be mentioned here that, according to observations made in tropical countries, atmospheric precipitation supplies more nitrate than the nitrification processes in the local soils.

All this still more clearly emphasizes the fact that the zone of weathering is permeated with oxygen and is a region of intense oxidation.

### 5. Reduction Processes

Simultaneously with the above reactions there occur reactions of the reverse kind. These new reactions are especially widespread in subaerial and subaqueous soils and result in the setting free of oxygen and the formation of reduced vadose minerals, rich in energy. The oxygen is utilized for the oxidation of other compounds.

From one point of view, the photosynthesis of organic compounds in green plants may be regarded as a reduction process, the oxygen of the absorbed $CO_2$ being set free. But quite apart from this extensive process, we can observe processes of the most diverse nature that are the direct antithesis of oxidation; for example, the microbiological processes of nitrification, oxidation of sulphur, hydrogen and methane, have their converses in denitrification, desulphofication and hydrogen and methane fermentation. We must consider these phenomena briefly.

Denitrification in the widest sense, *i.e.* the reduction of nitrates by microbiological reactions, proceeds in various ways. In some cases this reduction leads finally to the formation of ammonia, and in others to free nitrogen, but there are quite definite stages in these reactions. Thus, *Bacterium coli* extracts oxygen from nitrates to form nitrites, thus exactly reversing the reaction brought about by *Nitrobacter*. The nitrites thus formed react with amide compounds, lose their remaining oxygen and leave free nitrogen.

$$2HNO_2 + CO(NH_2)_2 = CO_2 + 3H_2O + 2N_2.$$

This decomposition of nitrous acid is in direct contrast to the work of nitrosobacteria, and the reduction of nitrates to ammonia is opposed to the nitrification of ammonia salts. The oxygen from the reduced nitrates and nitrites goes to the oxidation of organic compounds with the formation of $CO_2$ or organic acids. Thus, it is essential to note that *oxidation reactions are concomitant with denitrification.*

These processes occur to some extent in every soil and determine the fate of any nitrate that may be formed. The nitrates formed in the crust of weathering may be washed out in solution, find their way into loose sediments and be removed with the latter from the sphere of weathering, or

they may be taken up by plants and used in the formation of proteins or other nitrogen compounds. Finally, they may undergo denitrification and in this case yield up their oxygen for the partial or complete oxidation of organic compounds.

In many respects the process of denitrification is analogous to that of desulphofication which evidently takes place during the decomposition of organic matter under anærobic conditions when sulphates are present. The micro-organisms of desulphofication, *e.g. Spirillum desulphuricans,* are not necessarily connected with areas of pollution and dense human population as are many putrifying microbes. They are widely diffused and carry out their work in sea-water as well as in virgin tracts of the arid steppes and the frozen soils of the Siberian taiga, untouched by cultivation. The part played by these processes in the crust of weathering and in soils must be immeasurably greater than is at present realized.

The reduction of sulphates usually includes a sulphite stage and concludes with sulphides: hydrogen sulphide, metallic sulphides and in particular iron sulphide.

Desulphofication is especially intense in lagoons, estuaries, extensive areas of the sea, salt lakes and their shores, and wet sulphate solonchaks. The oxygen set free in the reduction of sulphates and sulphites, like that in denitrification, goes to the oxidation of organic compounds.

The hydrogen and methane fermentation, undergone by cellulose, are characteristic soil processes. They are carried out by specific micro-organisms (*Bacterium cellulosæ hydrogenicus* and *B. cellulosæ methanicus*). Since cellulose is always an important part of the organic residues occurring in soils, it is evident that such reactions may attain considerable dimensions. In these cases oxygen separates either in the form of $CO_2$ or as organic acids, *e.g.* butyric acid. Bearing in mind that the cellulose of the plant organism is built up from water and the carbon of absorbed $CO_2$, we see that there is a definite reversibility in these purely biochemical processes.

There is no information to suggest that the reduction of the oxygen compounds of iron and manganese is connected

with the activity of any particular micro-organism. It is true that these common processes are dependent on the decomposition of organic matter, which is in general microbiological, but the reduction itself is, or may be, a purely chemical reaction. The decomposition products of the organic matter (including hydrogen) take up oxygen from the mineral compounds, and especially the compounds of iron and manganese, and reduce them. The localities where such reduction processes are most strongly developed are swamp and lake deposits, moist meadow soils, river valleys, ground water horizons and buried soils. It is interesting to recall the well-known experiment of Potonié in E. Prussia. He submerged a sheet of rusty iron in lacustrine silt (sapropel) and after some time it was pulled up quite clean.

The compounds of iron and manganese in the lower states of oxidation are in general very easily dispersed and are therefore highly mobile. As they take part in the various changes in the crust of weathering, oxidation, translocation and again reduction, these *easily reversible* oxides take an active part, not only in the circulation, but also in the distribution of oxygen. In this connexion Cu, Co, Ni and Cr, although less widespread, resemble Fe and Mn to a certain extent.

We have now seen that both microbiological and chemical reduction together with oxidation are always elements of the complex process occurring in the zone of weathering. We have also seen that compounds of C, N, S, H, P, Fe, Mn, etc., having been reduced may be reoxidized. If to this we add the oxidation of vadose and juvenile elements and compounds (*e.g.* hydrogen, hydrocarbons, sulphur and other native elements, metallic sulphides, etc.), it is obvious that oxidation is one of the most important reactions and influences many of the further changes in the crust of weathering. It is true that a number of native elements are highly resistant to weathering and long remain in the unoxidized state. But these elements either do not play an important part in the zone of weathering (Pt, Au, Ir, Pd, Os and others), or like N give rise to oxygen compounds in some way or other in spite of their passivity and chemical inertness.

### 6. Juvenile Water: Hydration and Solution

Up to the present we have considered only those changes undergone by juvenile carbon dioxide. Another juvenile compound that contributes to the supply of oxygen in the zone of weathering is water. The view, formerly widely held, that the bulk of the gaseous products of volcanic action consisted of water, has recently been radically changed, although there is no doubt that juvenile water does find its way into the crust of weathering and later passes with the sedimentary rocks into the deeper shells of the earth. The fact that at the present moment in the history of our planet the main mass of water is concentrated in the hydrosphere[1] is only proof that completely reversible processes do not exist. It shows that the movement of matter in the earth's crust has a progressive component and that the formation of the hydrosphere is a definite phase in the life of the earth.

Water thus enters the zone of weathering in a variety of forms: the juvenile liquid water and steam from the deeper shells (volcanic and post-volcanic emanations, inclusions in rocks), in solid compounds (water of hydration of minerals, especially in metamorphic rocks), the vadose water of the hydrosphere, the vapours of the atmosphere. The great rôle of water in the zone of weathering is not limited to its participation in the cycle of oxygen compounds, but its part in that cycle is of no less importance than that of carbon dioxide.

Water, under the conditions obtaining in the zone of weathering, is a fairly stable compound *chemically* and carries out a vast amount of work in the transference and transformation of energy. This it does by changing its state of aggregation, by the mechanical transport of matter, by means of solution, hydration and absorption, by its inclusion in complex systems, to which it gives new stores of energy (*e.g.* ionization of salts in solution) or from which, vice versa, it takes away energy (the discharge of gases on absorption).

Nevertheless, there are, in the zone of weathering, processes that lead ultimately to the disruption of the water

[1] According to V. I. Vernadsky the water of the lithosphere amounts to less than 50 per cent. of that in the hydrosphere.

molecule. Water, just like carbon dioxide, is one of the foodstuffs of organic life and takes part in the photosynthesis occurring in green plants, being one of the materials used in the formation of carbohydrates (starch). But starch, as we have seen, undergoes decomposition during methane, or hydrogen, fermentation, and the union between hydrogen and oxygen is temporarily broken, and the oxygen goes to the oxidation of carbon. We say *temporarily* since both hydrogen and methane eventually become oxidized and may thus be considered ephemeral in the zone of weathering, even although they are somewhat more stable than nitric and sulphuric acids.

Of the other changes in which water takes part in the zone of weathering without the disruption of its molecule, hydration, including the formation of water of crystallization during the separation of salts from solutions, and the widespread process of solution, are of great importance. Hydration in the widest sense leads to the formation of oxygen compounds that are peculiar to the crust of weathering. The most important of these are the adsorption systems of the type $X.nH_2O$, *i.e.* compounds that adsorb water on their surfaces. The amount of water is not constant, and depends on the nature of the adsorbing surface and the vapour tension of the surrounding medium. Soils, swamps, lacustrine and marine deposits contain in abundance these colloidal adsorption compounds, among which are some that contain oxygen in forms other than water, *e.g.* $Fe_2O_3.nH_2O$, $SiO_2.nH_2O$, and others containing oxygen in the form of adsorbed water only, *e.g.* $FeS.nH_2O$. A very important property of these compounds is their ability in the course of time and under suitable conditions to change into simple, fairly stable, stoichiometric compounds with a definite water content. Thus, $Al_2O_3.nH_2O$ passes into gibbsite (hydrargillite) $Al_2O_3.3H_2O$, a crystalline mineral, which only gives up its water at a temperature of 200°C, and is one of the most resistant minerals characteristic of the crust of weathering. In the same way fairly stable hydrates of ferric oxide and many others are formed. The unhydrated varieties of these are found in the deeper zones of the lithosphere. No less innumerable are the

examples of salts separating out with different amounts of water of crystallization. Salt lake deposits and the saline bloom on the surface of the soil show many formations of the same kind. Natural sulphates of this type include: mirabilite (Glauber's salt) $Na_2SO_4.10H_2O$, gypsum $CaSO_4.2H_2O$, kieserite $MgSO_4.H_2O$, epsomite $MgSO_4.7H_2O$, iron sulphate $FeSO_4.7H_2O$, and others. Certain of the halides are also encountered: bischofite $MgCl_2.16H_2O$, carnallite $K_2Mg_2Cl_6.12H_2O$; and some carbonates: $Na_2CO_3.10H_2O$, $Na_2CO_3.H_2O$, $Na_2CO_3.CaCO_3.5H_2O$, and other more or less easily soluble salts.

In assessing the extent to which hydration, in the wide sense, occurs in the crust of weathering, it is necessary to remember that it may take place in many primary minerals *without any changes in their crystalline form.* For example, micas change into hydrated forms that retain the original crystal structure, differing only in their optical constants. Such hydration is doubtless one of the first stages in the weathering of the minerals, for the micas can then absorb gases ($CO_2$) and vapours more easily, and so decompose. The products of their decomposition also adsorb water and give rise to those adsorption compounds that are so characteristic of the crust of weathering. These are compounds of the clay type ($mAl_2O_3.pSiO_2.nH_2O$), colloidal forms of silica ($SiO_2.nH_2O$), hydrated varieties of ferric oxide ($Fe_2O_3.nH_2O$), etc.

The opposite of hydration is dehydration. The change of gypsum into anhydrite ($CaSO_4.2H_2O = CaSO_4 + 2H_2O$), soda into trona [$3(Na_2CO_3.10H_2O) + CO_2 = 2(Na_2CO_3 NaHCO_3) + 29H_2O$], glauber's salt into thenardite ($Na_2SO_4.10H_2O = Na_2SO_4 + 10H_2O$), and similar cases of the complete or partial loss of water of crystallization are common in the crust of weathering. Frequently, however, the *hydration of one compound takes place at the expense of the dehydration of another.*

Even the small rises in temperature on the surface of the earth brought about by the rays of the sun can apparently bring about the dehydration of certain hydrated organic and mineral compounds in the soil and the loss of water of

crystallization by certain salts and adsorbed water by colloidal compounds. Laboratory experiments have shown that a temperature of over 200° is required for the dehydration of manganite ($Mn_2O_3.H_2O$), but in nature the extreme slowness of the process is accounted for by the much lower temperature. In this case the axiom of mechanics which states that *the slower the process the smaller the amount of energy used up in unit time,* holds good. There is also reason to believe that the hydrated forms of ferric oxide may lose part of their water of hydration at the bottoms of deep basins under the influence of pressure and salt solutions. Nevertheless, dehydration can be considered as a phase in the general cycle of hydration characteristic of the zone of weathering.

The amount of hygroscopic moisture adsorbed by the clastic masses of the crust of weathering (*with their great active surface*) must reach immense proportions. Rain water percolates through the loose material saturating the minute colloidal particles, hydrating the mineral decomposition products, and finally collecting as streams or ground water. The crust of weathering acquires in this way an enormous amount of oxygen, quite apart from direct oxidation of its other components.

### 7. The Rôle of Water in Oxidation and the Distribution of Oxygen in the Crust of Weathering

No less important a part is played by water as an indirect factor in the process of oxidation. Without discussing in detail its catalytic effect in oxidation reactions,[1] it may be said that it is the dissolved oxygen that is the effective agent. Air dissolved in sea water has quite a different composition from that of the atmosphere. The dissolved air contains from 65 to 67 per cent. nitrogen and 33 to 35 per cent. oxygen, the difference being explained by the greater solubility of oxygen compared with nitrogen. Decrease in temperature results in an increase in the amount of dissolved gases and consequently of oxygen. This explains several

[1] Several oxidation processes, *e.g.* the rusting of iron, will only take place in the presence of water.

phenomena which clearly emphasize the rôle of water in the distribution of oxygen in the crust of weathering and so in the process of oxidation. Whilst swamps, lakes, lagoons, estuaries and parts of the sea bottom are well defined seats of reduction processes, *i.e.* of the decomposition of organic matter in the presence of but little oxygen, resulting in the formation of incompletely oxidized compounds, in many other cases there are very clear signs of complete oxidation. This evidently takes place at the expense of the dissolved oxygen. The wealth of hydrated ferric oxides in the sediments of the northern lakes in the Olonetz region (U.S.S.R.) is partly explained by the low temperature of the waters of these lakes and the consequent greater solubility of oxygen, and partly by the wealth of life and the biological forms of oxidation connected with it in the subpolar basins.

But an excellent illustration is given by the more highly oxidized compounds of the sediments in the deepest parts of the ocean, the so-called red muds. The essential constituents of this deposit are ferric and manganic compounds, distributed throughout the mass and in concretions. Of special interest in this connexion is the formation of the so-called *palagonite*, an oxidation and hydration product of a basic volcanic glass included in the red mud.

It would appear at first sight that at great depths measured in thousands of feet, the sea bottom would be almost devoid of free oxygen. Actually, the heavier and colder water of the comparatively shallow subpolar seas, containing more dissolved oxygen, diffuses into the deeper parts of the ocean basin. Since the water also brings $CO_2$, it evidently plays a part in the distribution of carbonates. This might have been concluded earlier from the discussion on carbonate formation.[1]

Thus water entering the zone of weathering from the deeper shells in the form of springs and volcanic steam, and from the outer shells as vadose solutions and rain, mixes with the other material. The movement of the solid masses of glaciers, surface and underground streams, capillary and pellicular moisture, and the movement of water vapour in the

[1] It should be noted that the stability of most carbonates decreases with the increase in the $CO_2$ content.

soil air under the influence of changes in temperature and partial pressure may be included.

Water leaves the zone of weathering in vadose compounds in sedimentary rocks and passes into the deeper shells or alternately by direct evaporation, run-off, and through organisms that use it as food, it reaches the atmosphere and hydrosphere. Its cycle in the zone of weathering is only a part of a much greater cycle that is definitely not closed, but is simply a link in a progressive process.

### 8. Transformation of Other Juvenile Oxygen Compounds. Irreversible Oxides

In addition to $CO_2$ and $H_2O$ a large number of other juvenile oxides occur in the zone of weathering in the form of minerals in igneous and metamorphic rocks, *e.g.* $SiO_2$ (quartz), $TiO_2$ (rutile, anatase, brookite), $SnO_2$ (cassiterite), $Al_2O_3$ (corundum, ruby, sapphire), $Fe_2O_3$ (hæmatite), etc.[1] These and analogous oxides interact to form salt-like juvenile compounds of the types: silicates, chromates, titanates, aluminates and ferrates, which are among the principal rock-forming minerals. To this type belong $ZrO_2.SiO_2$ (zircon), $FeO.Cr_2O_3$ (chromite), $FeO.TiO_2$ (ilmenite), $FeO.Al_2O_3$ (hercynite), $FeO.Fe_2O_3$ (magnetite). Finally, the main mass of both primary (igneous) and metamorphic rocks consists of aluminosilicates and silicates, *i.e.* salt-like compounds of silica, alumina, and the oxides of the alkali and alkaline earth metals, iron, manganese, etc. To this group of the commonest rock-forming minerals we must also add juvenile phosphates, arsenates, vanadates, niobates, tantalates, molybdates, tungstates, carbonates, etc. These free oxides and their complex compounds are introduced into the zone of weathering and there undergo a series of changes. Among these compounds silica ($SiO_2$) has a special place on account of its predominance and its properties.

Free juvenile silica, in the form of crystalline quartz, is very stable and remains practically unchanged if we exclude

[1] Sulphur dioxide ($SO_2$) is sometimes regarded as a juvenile oxide, but there is reason to believe that it is formed in the zone of weathering by the oxidation of sulphur vapours.

mechanical comminution, but the silica of complex silicates and aluminosilicates is a much more active substance. When it is set free from its compounds this silica adsorbs water, changes its state of aggregation and its degree of dispersion, enters into complex systems, even organic matter, and plays a most active part in the transformation of energy and other changes in the crust of weathering. Nevertheless, whatever changes silica may experience, it is never decomposed, and the union between Si and O is never broken. It may therefore be asserted that the oxygen that enters the zone of weathering in combination with silicon, retains that union the whole time it is in this zone and takes no part whatever in the oxidation of other elements. Silica is a good example of the oxides that are irreversible in the zone of weathering. The oxides of titanium ($TiO_2$) and zirconium ($ZrO_2$) behave in a like manner.

Alumina may also be included in this group, for free juvenile alumina in the form of corundum and its coloured varieties may be considered fairly stable. But the alumina of complex compounds appears to break up on weathering, and several vadose salts of aluminium (*e.g.* sulphates) are known in the crust of weathering. These give the $Al'''$ ion in acid solutions, and so there is the possibility that there may be others, even adsorption systems, in which the union between Al and O is broken. It is doubtful whether such systems could ever be stable, and we can therefore assume that the bulk of the oxygen entering the zone of weathering in the form of free and combined alumina retains its union with aluminium while it is in that zone. As seen above the behaviour of the group of oxides headed by $Fe_2O_3$ and $MnO_2$ is different. Their juvenile and vadose compounds are indistinguishable, and they are typical reversible oxides, which easily change their state of oxidation. Cases are known in which ferric compounds have been completely reduced to vadose native iron.

Finally, the oxides of the alkalis and alkaline earth metals form a special group. They never occur in the zone of weathering in the free state, but appear in the form of complex compounds, mainly silicates and aluminosilicates

(feldspars, micas, augites, hornblendes, olivines, chlorites, etc.). Notwithstanding the ease of oxidation of the corresponding metals, there are times when their union with oxygen is broken. This may take place during the reduction of certain vadose salts, *e.g.* as a result of denitrification or desulphofication. These processes lead not only to the formation of nitrites and sulphites, but to sulphides also in the second. The formation of vadose halogen salts can also be included in this group of reactions.

Considering that the formation of halogen salts is predominantly the result of exchange decomposition reactions in which the halogens combine with the alkali metals in oxy-salts, the anions of which are taken up by the alkaline earths, iron, manganese and other elements, which give reversible oxides, it follows that there is a tendency at the present moment towards the *accumulation of the mineral oxidants of organic matter.*

The hydrochloric and hydrofluoric acids in volcanic gases supplement the halogen salts in the crust of weathering, and displace the oxy-anions which pass into less stable unions. This fact lends support to the above hypothesis.

The complex oxygen cycle in the zone of weathering is represented in *Fig.* 2. The changes undergone by the irreversible oxides ($SiO_2$, $Al_2O_3$) are not included, since they are considered in the subsequent chapter.

## 9. The Carbon Cycle

In considering the cycle of oxygen compounds we ought to have touched on nearly all the other important elements in the zone of weathering, since oxygen combines with them in some form or other. But since our attention was concentrated primarily on oxygen it was not possible to dwell to any extent on their history, and we must now rectify that omission.

The most important primary forms of carbon in the zone of weathering are the hydrocarbons ($CH_4$, $C_2H_4$) and oxides of carbon occurring in volcanic and post-volcanic gases, and minerals of igneous and metamorphic rocks: carbonates (primary calcite), carbo-silicates, graphite. Among the less

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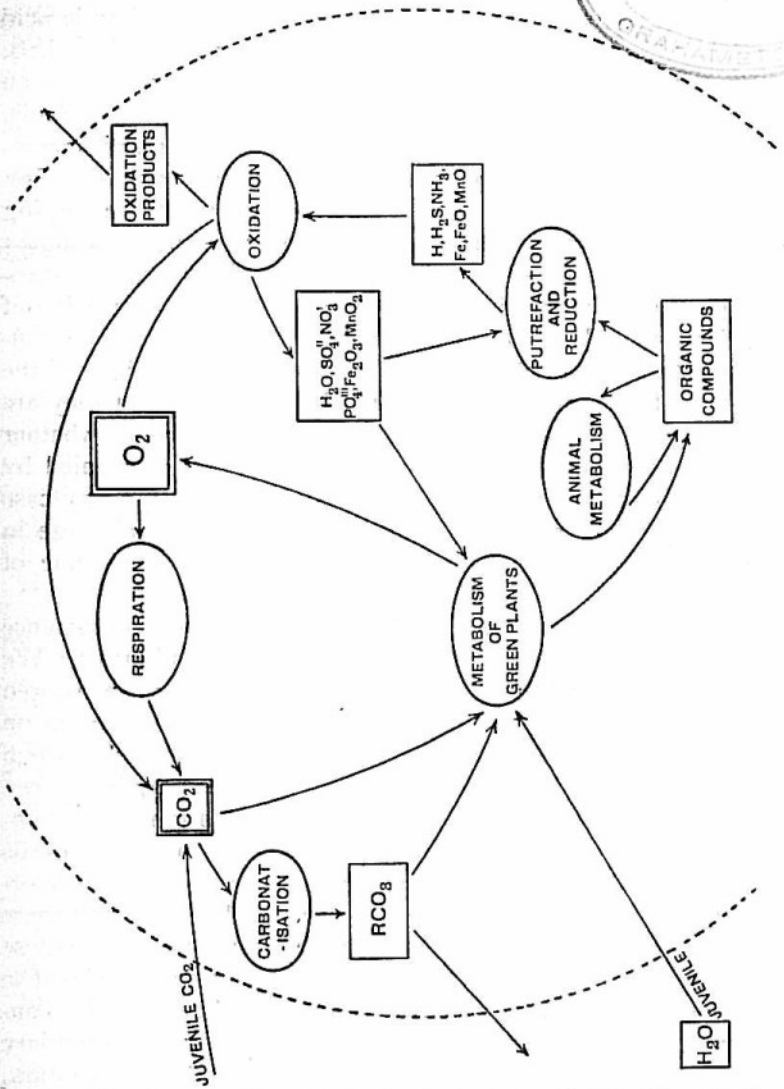



FIG. 2.—Fundamental Phases in the Cycle of Vadose Oxygen Compounds. Ellipses represent processes, rectangles—products. The arrows cutting the broken line show the juvenile and phreatic compounds of oxygen entering the crust of weathering and the vadose compounds leaving it.

common compounds are formaldehyde ($CH_2O$), formic acid ($CH_2O_2$), and the metallic carbides (of iron and nickel). Juvenile carbon dioxide has already been mentioned as an oxygen compound. All the other primary carbon compounds, with the exception of carbonates, consist either of incompletely oxidized or oxygen-less compounds, and the first change they will undergo on entering the crust of weathering will be oxidation. This is brought about either directly or through the action of organisms, predominantly microorganisms, but the final result is the same—the formation of carbon dioxide. This change, however, must not be considered as absolutely essential. The relative stability of the various forms of carbon[1] will not be discussed, but they are all oxidized to a greater or less degree, depending on whether they enter that part of the zone of weathering occupied by the biosphere or remain in the deeper regions. In any case it is correct to regard carbon dioxide as the initial stage in the transformation of carbon compounds in the zone of weathering.

In previous sections we have shown the wide occurrence of carbon dioxide in the zone and crust of weathering. We used this as an illustration of the distribution of an oxygen compound. We must now consider the two processes on which this distribution depends and during which carbon dioxide enters the carbon cycle. These two processes are: (1) the formation of carbonates, (2) the formation of the complex organic compounds of living matter by photosynthesis in green plants and chemical synthesis by certain lower organisms. We have already discussed carbonates, and there is no doubt that the contemporary accumulations of vadose carbonates in the zone of weathering cannot be considered to be inert. They take part in innumerable partial cycles connected with the transformation of energy (solution, secondary precipitation, crystallization, organization, decarbonization, etc.). At the same time the 30,000 billion tons of carbon dioxide combined in limestones point to a certain cessation in the tempo of the evolution of carbon compounds and force us to consider $CaCO_3$ as a carbon compound that is compara-

1 Graphite is especially stable, but on comminution it is oxidized.

tively stable in the zone of weathering and one that removes a certain part of its carbon to the deeper shells of the earth.

In order to elucidate the principal phases in the changes undergone by the organic compounds of living matter we must consider three important properties of the latter: metabolism, reproduction and adaptation. The first conditions the accumulation and alteration of organic compounds within the organism. These compounds are formed in the organisms of green and lower plants by chemical and photosynthesis, and after undergoing definite changes they are utilized by animals and parasitic and saprophytic plants as food and increase in quantity. Metabolism and reproduction result in an accumulation of the organic compounds, whilst the adaptation of the organism to its surroundings and their changes leads to a steady development and a wide distribution of new forms. At the present stage in the history of the earth, living organisms occupy the whole of the hydrosphere, the upper part of the crust of weathering and the lower layers of the atmosphere. In the last two shells the limits of life are not very definite, and our ideas of them change with the progress of investigations and the accumulation of new facts. In this connexion it is interesting to note that in contradiction to the general view that the distribution of organisms in the soil is confined to a few metres, the recent investigations of Brodsky[1] have shown the presence of living organisms (rhizopods) in the deep horizons of ground water. According to Nansen, water, formed on the surface of polar ice by the heat of the sun, contains micro-organisms. In the same way, we are beginning to doubt the existence of *absolute deserts*, *i.e.* areas entirely without life. The indefiniteness of the boundaries of the sphere of life on the one hand, and the unceasing evolution in the organic world on the other, leads to the suggestion that at the present stage in the earth's existence the amount of living matter is increasing and is extending the limits of its distribution. The amount of carbon in living matter at present is measured in thousandth parts of its total quantity in the earth's crust, but in the

[1] A. Brodsky, The Fauna of the Kara-Kum Desert, *Trans. State Univ. Middle Asia*, Series XIIa, pt. 5, Tashkent, 1929.

future it obviously ought to increase at the expense of the juvenile forms of carbon. Life began to develop on our planet at a certain historico-geological moment, and there is no reason to suppose that it is becoming extinct, so that the suggestion we have made receives still more support.

The organic compounds of living matter undergo combustion and are changed to $CO_2$ in the respiratory processes during the life of the organism. This combustion does not cease on the death of the organism, but is replaced by microbiological or direct oxidation, which affects not only its remains but also its excreta during life. All this material, remains, excreta, etc., we will call organic residues. Depending on where they accumulate and the amount of oxygen available, organic residues undergo either humification or putrefaction. Putrefaction results in the formation of incompletely oxidized products ($CH_4$, CO, $H_2$, etc.), which may subsequently undergo further oxidation. This incomplete decomposition of organic remains is extremely important. A certain proportion of the products never reach the end point ($CO_2$), but remain in various intermediate stages or even in an unaltered state, and are so carried into the deeper zones of the lithosphere to undergo further changes. The resistance to oxidation and decomposition depends on the nature of the organic compound and the manner of accumulation. As far as individual compounds are concerned, those that give way to oxidation and decomposition most readily are protein substances, aminoacids, acid amides (asparagine, leucine), amines, sugars, starch, organic acids, and in general those compounds which form the most accessible foods for micro-organisms. Cellulose and fats are difficult to decompose, more difficult is lignin, the corky matter in which plant remains are rich, while most difficult of all are tannins, resins, waxes, chitin, etc. Amber, and the chitin of certain brachiopods, preserved in sedimentary rocks from the beginning of the Cambrian period, clearly demonstrate the stability of the last group of substances. In Wollny's experiment peat freed from the waxy matter enveloping it decomposed twice as quickly as the untreated material. But under suitable conditions even proteins can

be preserved for a long time. The intensive accumulation of organic residues in the limited space, which decreases the surface in contact with oxygen, assists in their conservation, but in this case no small part is played by the form of the accumulation itself.

## 10. Forms of the Accumulation of Organic Residues

The many forms in which organic matter accumulates in the crust of weathering may be divided into three main types: (1) humus, (2) peat, (3) sapropel.

By *humus* we understand the accumulation of organic residues (plant and animal) in the surface of the land and in the uppermost layers of the lithosphere. For the most part this form of accumulation undergoes oxidation.[1] Being constantly supplemented with new material and evolving the end-product of oxidation, $CO_2$, the content of which may reach 10% in the soil air, humus includes in its composition both unaltered (fresh) and little changed organic remains, as well as a large number of compounds of varying composition and representing various stages in the decomposition. It is very important to observe that some of these intermediate products are extremely active. They may become mobile and absorb the solutions circulating in the crust of weathering; they may combine with the mineral elements forming new mobile systems. This is important in showing that the carbon compounds, formed in an organism, *do not simply accumulate or burn away after the death of the organism, but, before reaching the end-stage ($CO_2$) show great activity and take part in the cycles of other elements in the crust of weathering.*

Not so long ago this active part of humus or *active humus* was regarded as the combination of specific organic acids, but at the present time the views on the nature of humus have undergone a fundamental change. The presence of organic acids in humus cannot be denied, because many organic acids are characteristic of living organisms, while

[1] In dealing with the decomposition of organic residues in nature we can speak only of the *predominance* in some cases of oxidation, in others of putrefaction, for during almost any decomposition both processes are at work, increasing one moment and decreasing the next.

others are necessary products of certain decomposition processes taking place in the soil (*e.g.* hydrogen or methane fermentation). The properties of active humus, however, are explained mainly by its colloidal state. The colloidal nature of this part of humus is shown by its ability to be peptized, *i.e.* dispersed in the solution circulating in the soil and subsoil; by its adsorptive properties, *i.e.* the ability to hold on its surface not only compounds, but also ions, from solution; and by the phenomena of coagulation, the formation of gels, and, with other components of the disperse phase, coagels. These properties have been demonstrated in the laboratory and may be confirmed by a large number of observations on the natural products. In the great majority of these experiments and observations the humus colloids prove to be electronegative, which explains their ability to adsorb cations from solutions. This electronegative character, and the analogy existing between the adsorption complex containing adsorbed ions and true salts, were the reason for the development of the theory of organic acids. As echoes of this now forsaken theory we still have such terms as humates, crenates and apocrenates, which were taken to be salts of definite organic acids, while they are actually organic hydrosols and hydrogels containing adsorbed cations (Ca, Mg) or complex coagels (iron humates), all of which can be separated from soils by various methods. It is necessary, however, to state that under certain conditions, *e.g.*, by the action of alkaline solutions (NaOH, KOH) of definite concentrations on the so-called "huminic acid," a true solution is obtained as has been shown by Ostwald and Rodiger. This, of course, does not prove that huminic acid is a definite stoichiometric compound, but it may be assumed that it is a mixture of various organic acids. In the experiments mentioned the huminic acid was artificially prepared from one carbohydrate, whereas the organic adsorption complex of soils does not have a constant composition and is generally much more complex. It may be assumed that it contains organic acids, but in the majority of cases its properties ought to be put down to its colloidal nature. It is well known that the sign and size of the charge on the disperse

phase is determined not only by its nature but also by the properties of the solution (hydrion concentration). Cases of the reversal of the charge on colloids are also known. Thus, when we speak of the electronegative character of soil colloids we mean that the majority of the changes that they undergo in nature take place under conditions which make them assume an electronegative charge.

In discussing the compounds and adsorption systems that comprise active humus and whose existence is sufficiently authentic we shall represent the soil organic adsorption complex by the symbol (Hum . . . nOH′)nH˙, in order to show the electronegative character of the colloid.[1] As we have already mentioned, its composition is fairly complex and undetermined. Doubtless its main sources are slowly decaying organic residues, such as cellulose, but the presence of nitrogen in the adsorption complex shows that other compounds have a part in its formation. Humus is slightly peptized by weakly acid, and strongly by alkaline solutions. Such solutions are known in the crust of weathering and, as we shall see shortly, are characteristic of definite regions. Humus sols in weakly acid solutions are characteristic of the water of bogs (swamps), lakes and even rivers in the taiga region of Eurasia and N. America and in moist tropical countries. When sesquioxides and dissolved humus are present in certain proportions mixed sols are formed. If the proportions are altered coagulation may ensue with the formation of coagels of humus with the hydrated oxides of iron and aluminium. This can be demonstrated experimentally by changing the proportions of the various sols, the action of electrolytes, mechanical coagulation, etc. Observations in nature prove the existence of natural coagels of humus and iron oxide (FeHum). A number of iron ores in the crust of weathering (bog and lacustrine ores) have, it seems, just such an origin, and the places in which they occur

[1] This symbol actually expresses only the surface of the hydrated molecules of the colloidal micelles. In a simplified form these molecules may be conceived to contain a double layer of ions. The inner layer, closely bound to the surface molecules, determine the sign of the charge ($OH'$) of the colloid, and the outer consists of the adsorbed ions ($H^{\cdot}$), which are replaceable. It is possible that the inner layer is made up in this case not of hydroxyl, but of carboxyl groups (COOH).

are closely connected with that part of the crust of weathering where organisms and humus play a fairly active part. Natural humus sols and their gels and coagels show how the distribution and secondary deposition of those carbon compounds that make up active humus may be brought about. A considerable amount of active humus dissolves in the alkaline solutions that are characteristic of saline soils and subsoils, but these solutions are not stable, and the sols of organic colloids do not migrate to any extent in this form. They percolate to no great depth in the subsoil. Since these solutions have a high colouring power, even a comparatively small amount of total humus, and of the active variety in particular, can colour a soil almost black.[1]

From the adsorption compounds of humus we may single out the adsorption complex saturated with metallic cations, among which calcium may be considered the most important. This is a weakly dispersed system, difficult to disperse in water or in solutions, and apparently formed as a result of the coagulation of humus sols with electrolytes, principally Ca salts. It is widespread in soils, and is especially stable in the little leached soils of continental countries. On the other hand, the system in which sodium is the principal cation is easily dispersed and is evidently an extremely important constituent in the above-mentioned alkaline solutions. The system containing adsorbed hydrogen is moderately easily dispersed and is characteristic of acid soil solutions. There is no doubt that the number of organomineral adsorption systems in nature is much greater and their composition much more complex than would appear from experimental work on the formation of complex sols (Fe-, Al-, and even SiAlHumus).[2] The nature of these possibly analogous adsorption systems is at present far from being clear.

In general all organomineral compounds and humus systems are unstable, not only because of their colloidal

[1] Personal observations on many valley meadow soils of the southern steppe rivers have shown that extremely black soils may only contain 2-3% humus.

[2] Buzagh's experiments have shown that kaolin may be peptized in alkaline solutions of humus, *Kolloid-Ztschr.*, 1928, **44**, 156-162.

nature, but because the organic portion is continually decomposing under the natural conditions of humus accumulations. They are ever present only because there is a constant addition of new material from which they may be formed, but the individual compounds may be classed as ephemerids of the crust of weathering on account of their short existence. They are highly endothermic compounds which are not in equilibrium with the thermodynamical conditions of the crust of weathering.[1] It is thus natural that no great accumulation of humus is ever formed, and the greatest content of organic compounds reaches 20-30% only. In cases where the amount of organic matter exceeds these limits we are dealing with something quite different—a transition to peat-forming accumulations.

### 11. Peat Formation. Sapropels and Sapropelites

Peat-forming accumulations are nearly always connected with lacustrine-swamp conditions, *i.e.* with an excess of water that secures on the one hand the development of hydrophilic plants, and on the other is not so excessive or of such a nature that plant life is almost impossible (running water, saline lakes, etc.). Peat formation is the result of the progressive accumulation of organic and especially plant remains, and the content of organic matter reaches such values (70-90%) that the mineral elements of the crust of weathering play a very subordinate part.

The main reason for the progressive accumulation of organic residues is that the amount of material added exceeds that removed by decomposition and mineralization. This in its turn depends on (a) the rapid growth and reproduction of the plants, (b) the excessive development of such organic compounds as are difficult to decompose, and finally (c) the development of such conditions in the medium that the life-activity of micro-organisms is reduced to a great extent or completely extinguished.

The significance of these different causes is variable, and we thus have different kinds of peat accumulations. The process of peat moss formation and its growth is the

[1] Cases of rapid decomposition of organic residues are found in the so-called podzolized and related soils of moist tropical countries.

result of the death and burial of plant remains of the greatest variety, yet the specific peat formers which give rise to the main bulk of the accumulations are comparatively few in number. Among them are rushes, sedges, horse-tails (*Equisetum*), etc. Woody plants are represented by pine (*Pinus sylvestris*), and its races specific to peat mosses (*e.g. P. sylvestris var. pumila* Abol. or f. Wilkommi), birch, which has also races peculiar to peat mosses, black alder (*Alnus glutinosa*) so characteristic of valley swamps, and spruce. The mosses are principally *Sphagnum* spp., and the group of *Hypnum* mosses, among which an especially important part is played by the *Amblystegiaceæ*. Corresponding to the part played by any of these plants in the formation of peat accumulations, it is possible to distinguish the peat of which the latter consist and the further changes it may undergo.

The most important peat formers are the sphagnum mosses, whose accumulations are widely diffused over the taiga region of Eurasia and North America. The depth of these accumulations sometimes amounts to tens of metres, while their areas may be quite considerable, reaching several square kilometres. Once sphagnum mosses invade an area of suitable hydrothermic and soil conditions (poverty in mineral nutrients, especially Ca) they develop and spread extremely rapidly. They have a high hygroscopicity and can absorb up to fourteen times their own volume of water, retaining this property even after their death. Thus, sphagnum remains form an excellent substrate for the development of future generations. Owing to this property the sphagnum cover easily spreads from its centre of origin and does not even stop at fairly steep slopes, as can be seen in the mountain forest zone of Eastern Asia (Amur region).[1] In competition with other vegetation it is usually victorious, and under its cover lie buried great forests, the area conquered being transformed into a limitless peat moss.

Such peat mosses consist of an accumulation of peat formers in which the three conditions specified above are completely fulfilled. There is an extremely rapid multiplica-

[1] Sphagnum peat is also to be found on hill slopes in Britain.

tion and development of organisms, a predominant part of the mass comprises cellulose and waxy substances, and the amount of protein is insignificant. Organic acids that are formed on putrefaction cannot obtain bases for their neutralization. The consequent comparatively high acidity inhibits bacterial and, in general, microbiological activity, and certain forms of mossy peat are so sterile that they can be used in surgery as aseptic dressings in place of sterilized wadding. This lowering of microbiological activity assists still more in the conservation of organic residues.

Other kinds of bogs and swamps (sedge, rush, hypnum, pine, birch, etc.) are much richer in microflora and microfauna, and in such cases peat formation begins when the first condition is fulfilled. Thus, rush swamps do not always give rise to peat and, under certain hydrothermal (climatic) conditions, exist as periodic formations, and through time almost completely disappear (*e.g.* the swamps along steppe rivers). Nevertheless, all types of peat mosses consist of an accumulation of residues predominantly rich in slowly decomposing organic compounds (cellulose, lignin, corky tissues), and poor in proteins. This is one of the features distinguishing peat from sapropel.

Types of swamps and peat mosses alter not only in space, but also in time, and often retain evidence of the succession of one type after another.

Since every peat-forming deposit of organic remains undergoes decomposition to some extent it is natural that it should to a corresponding extent give rise to the intermediate products of oxidation, and in particular to the constituents of active humus. The organic sols of river waters have their origin mainly in peat formations. The main mass of peat retained in the crust of weathering eventually becomes buried in the deeper parts of the lithosphere, and there undergoes transformation into various kinds of coal (*e.g.* the remains of woody plants give forms of coal, *e.g.* lignite). This process can hardly be considered microbiological. It is quite possible that the microbiological processes of humification are to some extent preparatory to coal formation, but coal formation itself takes place in zones

devoid of organic life, and it must be supposed to be a process approaching that of metamorphism. It is possible that the same reactions occur here as take place in the preparation of wood charcoal only much more slowly and under great pressure. *In fine,* peat mosses are forms of carbon accumulation, in which the carbon leaves the cycle of the weathering, thus completing a phase in a much greater cycle.

Another form of accumulation of organic matter is *sapropel, i.e.* silts, frequently rich in organic compounds, which are formed on the bottoms of various water basins: lakes, lagoons, estuaries, and even in some parts of the sea bottom. The remains of phyto- and zooplankton, algæ, etc., that accumulate there are somewhat richer in protein and fatty substances. Decomposition takes place in the presence of but little oxygen and is therefore somewhat akin to putrefaction, and as a result there are formed various hydrocarbons and products of the reduction of mineral compounds (compounds of ferrous oxide and ferrous sulphide are especially characteristic of sapropels used as medicinal muds). Free organic acids are not as a rule formed, and the reaction of the medium is usually alkaline. Of the compounds more resistant to decomposition, fats are somewhat important, but in general the progressive accumulation of organic remains in sapropel is governed by the intense development and multiplication of organisms. It does not always occur, and cases may be observed in which the sapropel is completely mineralized. In other cases the viscous jelly-like sapropel in which the organic remains are thoroughly intermixed with mineral silt may become buried under new formations, accumulations and water-borne material, and finally converted into sapropelite, or, in the case of a sandy mineral base, into sapropsammite.

Sometimes different forms of sapropel and sapropelite underlie peat mosses or are interlayered with them, indicating that the peat moss has been formed in a lake basin or is the result of periodic fluctuations between lacustrine and bog conditions. With the passage of time sapropel may become bituminized and so provide the beginnings of bituminous shales. Upholders of the theory of the organic evolution of petroleum regard sapropel as its primary source.

## 12. The Nitrogen Cycle

The cycle of nitrogen compounds in the crust of weathering is very closely connected with that of carbon. The juvenile sources of these compounds are principally volcanic discharges of nitrogen which may sometimes represent quite a considerable part of the gases evolved. The gases saturating certain mineral springs are especially rich in nitrogen, while a much smaller proportion is present in the gaseous inclusions of igneous rocks. The juvenile forms in which nitrogen is given off are not confined, however, to free nitrogen, and among the others are compounds, such as $(NH_4)_2CO_3$ and $NH_4Cl$, which are sometimes found in the discharges of active volcanoes (alkaline fumaroles). At the present stage in the life of the earth the crust of weathering has a large supply of vadose nitrogen in the atmosphere, which has been formed in bygone ages. The accumulation in that shell is extremely stable under the conditions obtaining there. Nevertheless, within the biosphere free nitrogen is brought into circulation by its fixation by a special group of vegetable organisms, and this marks the beginning of the main cycle of nitrogen compounds in the crust of weathering. The fixation of free nitrogen in the biosphere and in the crust of weathering, and its assimilation and further transformation within the organism to protein and other organic compounds, is carried out by a number of free-living micro-organisms. Among the aerobic types are *Azotobacter chroococcum, A. agile,* and among the anaerobic is *Clostridium pasteurianum.* Another group is represented by the nodule bacteria which live on the roots of plants of the *Papillionaceæ* family and form the peculiar little lumps on their roots. This group consists of various races of *B. radicicola.* According to several authors the property of fixation and assimilation of free nitrogen is also held by certain lower fungi (*Penicillium glaucum, Aspergillus niger,* and others). It is obvious that this very important phenomenon—the entry of free nitrogen into the composition of organic compounds—takes place almost entirely in the soil, *i.e.* in the crust of weathering.

A further important phase in the nitrogen cycle is the

ammonification of organic nitrogen during putrefaction, fermentation and other decomposition processes. In these a large number of micro-organisms take part. Especially characteristic is the fermentation of animal urine in which form the organism gets rid of a considerable part of its protein nitrogen. The reaction takes place according to the equation :—

$$CO(NH_2)_2 + 2H_2O = (NH_4)_2CO_3.$$

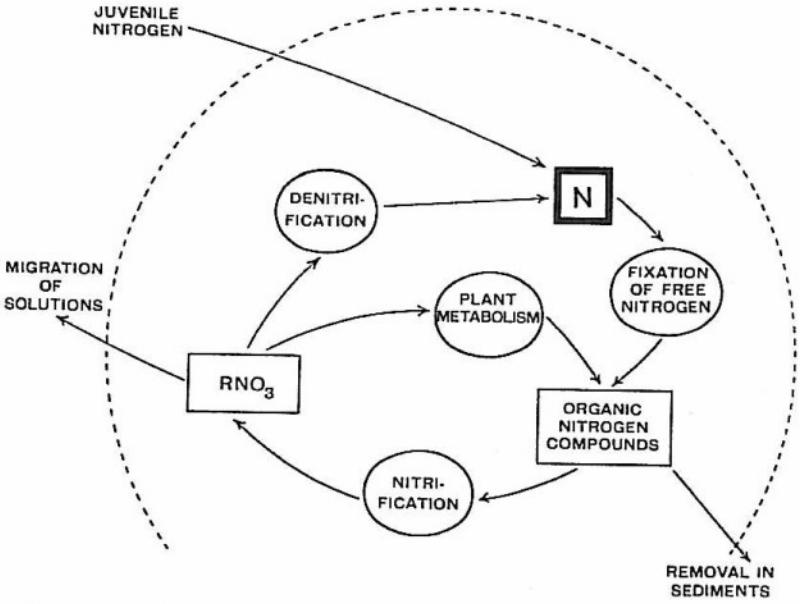



FIG. 3.—The Cycle of Vadose Nitrogen Compounds. (See notes to *Fig.* 2.)

The ammonium carbonate may then be decomposed with the formation of free ammonia :—

$$(NH_4)_2CO_3 = 2NH_3 + CO_2 + H_2O.$$

This decomposition is the reason for the ammoniacal smell that is so characteristic of putrefying urine. We have already learned the further fate of ammonia compounds during the discussion of nitrification and denitrification (pp. 35*ff*). In these pages we discussed the reverse of the above cycle in the form of the denitrification process and saw that part of the cycle is invariably connected, on the one hand,

with the metabolism, development and reproduction of organisms, during which the stores of organic nitrogen compounds increase, and, on the other, with decomposition processes (putrefaction, fermentation, etc.), in which the nitrogen returns to its original form (N, $NH_3$). It is only necessary to add that a certain part of the nitrate forming the mineral food of plants enters the zone of weathering directly from the atmosphere as a result of the oxidation of atmospheric nitrogen by electrical discharges.

It is also extremely important to note that not the whole of the organic nitrogen reaches the final forms of free nitrogen or ammoniacal compounds that are formed as a result of decomposition. A considerable part in the form of compounds that are incompletely decomposed leaves the crust of weathering in peat, coal and sapropel. The presence of nitrogen in the gases emanating from coal measures substantiates this, and at the same time shows how nitrogen can return to the crust of weathering. It may be mentioned that the presence of nitrogen in petroleum is a fact strongly supporting the organic theory of its origin. The general scheme of the nitrogen cycle in the crust of weathering is given in *Fig.* 3.

## 13. Plant Nutrients (Organogens). The Hydrogen Cycle

The elements oxygen, carbon and nitrogen, whose cycles in the crust of weathering we have just discussed, are referred by botanists and agronomists to the group of organogens, *i.e.* elements without which organisms cannot exist. Others belonging to this group are hydrogen, potassium, calcium, magnesium, iron, sulphur, phosphorus. The remainder of the elements, and even those that usually occur in plant ash (Na, Cl, Si), are not considered to be *absolutely necessary* for the life of plant organisms, although many of them are justly recognized as taking part in some or other biological process (growth stimulants, protective action, etc.). It should be remembered that the distinction between organogens and the other elements of the lithosphere was arrived at as a result of experiments with water cultures.

These experiments show that when the contents of K, Ca, Mg, Fe, S and P were adequate, plants develop normally and show no need for any other elements.

To assess the value of such experiments and conclusions it is necessary to remember that, as a rule, no account is taken of the mineral elements already present in the seed. It is true that their content cannot be great, but the importance of any element in biological processes cannot be determined solely by the amount present, and sometimes the most minute quantities can influence important reactions (*e.g.* by catalytic action).

But apart from this any definite conclusion from the results of water cultures can only be made in these terms: *for the development of individual plants, isolated from their natural environment and nourished under the artificial conditions of water cultures, no elements other than those organogens specified above are necessary as mineral nutrients.* It does not follow, however, that these artificially grown plants would behave in the same way and play the same part as their kin growing in their natural environment, if they were included in the complex cycle of the biosphere. Nor does it follow that they would not have fallen by the wayside in the struggle for existence, that their organisms would not have shown some other influence on parasitic organisms, herbivorous animals or the saprophytes that feed on their residues. It must be remembered that the intimate part played both by organogens and the other elements of the lithosphere in organic life is still obscure. Recent investigations have shown the great importance of certain non-organogens in animal and plant organisms (*e.g.* Si and Mn), and we must conclude that water culture experiments, whilst being of great interest in the isolated culture of individual plants, do not and cannot shed any light on the importance of, and the part played by, the individual mineral elements in the biosphere. The limitation of the group of organogens to those elements we have mentioned is extremely arbitrary. It is sufficient to state that the study of the physiology of animals has increased the number of organogens, which now include Na, Cl, As and I. The number will no doubt be

further increased as science develops, and any existing limitation can serve little purpose in the understanding of the interaction between organic life and the elements of the lithosphere.

Being guided by the quantitative participation of the elements in the composition of living matter we must distinguish first of all a group of four elements: C, O, N and H, which make up its main bulk. The remainder are measurable only in tenths, hundredths or even smaller parts. Exceptions for certain groups of organisms are Ca and Si, but the organogens cannot be separated by merely arranging the components in increasing or decreasing order, and in many individual cases the non-organogens predominate. Since the fate of certain organogens in the crust of weathering is closely bound up with that of other elements we shall adhere to an order governed by that connexion in the further discussion.

The discussion of the cycles of the principal organogens in the crust of weathering may be considered completed if we recall that the juvenile forms of hydrogen (free hydrogen, hydrocarbons, water), the oxidation of free hydrogen and methane (p. 37) and its reduction during hydrogen fermentation (p. 41) have already been discussed, and that its most stable form in the crust of weathering is water, which takes part in the reactions of photosynthesis in plants.

CHAPTER III

# THE SILICON, ALUMINIUM AND IRON CYCLES

## 1. Juvenile Forms of Silica. The Silica of Silicates and Aluminosilicates

The most important elements after oxygen, in decreasing order of their contents in the earth's crust, are silicon and aluminium, which are closely connected during many phases of their respective cycles.

Throughout the great majority of juvenile sources of silicon, made up of the various forms of primary quartz, the innumerable groups of ortho- and metasilicates, and the still greater group of aluminosilicates, there are few compounds in which silicon is not united to oxygen. Exceptions are found in volcanic emanations of $SiF_4$, and its salts found in lavas near to acid fumaroles. These salts include *hieratite* ($K_2SiF_6$) and *cryptolyte* [$(NH_4)_2SiF_6$]. Such compounds are very unstable under the conditions obtaining on the earth's surface and are quickly broken down and changed to some other secondary minerals in which silicon becomes united to oxygen. This is a very strong union and is never broken in the crust of weathering. It is therefore natural to consider, not the cycle of silicon, but that of *silica*.

Primary quartz is such a stable substance and undergoes so little alteration that it may be considered to be quite passive in the zone of weathering which it leaves in the same form as that in which it entered. Individual cases of the solution of the quartz of certain granites (Ural) belong to processes that can hardly be considered weathering. It is otherwise with the silica that enters into the composition of silicates and aluminosilicates. Both experiment and observation show that during the weathering of these minerals and during their attack by water, especially carbonated water, their silica is dissolved out to some extent. This explains why the vadose solutions circulating in the crust

of weathering, *e.g.* the water of springs, rivers, wells, etc., nearly always contain a certain amount of dissolved $SiO_2$ *in some form or other*. Sometimes its content exceeds that of dissolved carbonates, chlorides and sulphates, and may exceed 50% of the total dissolved matter.

The expression *in some form or other* is intentionally emphasized, for the nature of the silica solution cannot always be determined with accuracy. Molecular disperse solutions of silica are unknown. Recent investigations[1] have shown that extremely pure silica sols are neutral and their hydrion concentration does not exceed that of the purest laboratory water. Prolonged electrodialysis results in the coagulation of such pure sols, but they may be readily peptized by the addition of small quantities of hydrochloric acid (final concentration 0·01-0·1 N.).

The electronegative nature of silica sols is shown by their stability in alkaline solutions (protective action of $OH'$) and by many coagulation phenomena connected with the adsorption of cations from solution. Nevertheless the fact that silica sol is also stable in weakly acid solutions indicates its strongly hydrophilic nature and its correspondingly high degree of dispersion. The formation of silica sols during the weathering of silicates is fairly satisfactorily explained by a hydrolytic reaction of the type:—

$$Na_2SiO_3 + H_2O \rightleftharpoons 2Na' + 2OH' + coll.SiO_2,$$

and then

$$coll.SiO_2 + H_2O \rightarrow [SiO_2 \ldots OH']H'.$$

Actually the process is both complicated and intensified by the presence of $CO_2$, by the formation of carbonates, and finally, inasmuch as cations are present, by the formation of adsorption systems.

It follows that great importance must be attached to the mechanical comminution of rocks which, although lowering the mass of individual particles, leads to a considerable rise in their specific surface. The rate of water adsorption and other reactions of colloidal systems also increase in consequence.[2]

[1] V. A. Kargin and A. J. Rabinovich, "Colloidal Electrolytes," *Faraday Society*, 1935.

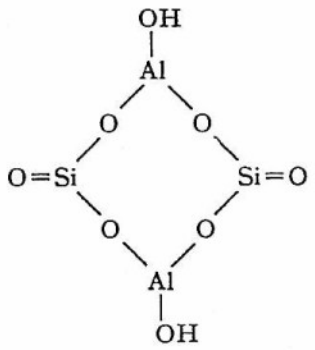
[2] A. Gabriel, Verwitterung der Mineralien durch Adsorption, Jena, 1909. A discussion of the complex reactions occurring on the surface of minerals.

It should be mentioned, however, that the union between silica and other elements in juvenile minerals is by no means uniform, and consequently the formation of free active silica takes place at varying rates. It is thus necessary to distinguish simple and complex silicates (aluminosilicates). In simple silicates, *i.e.* salts of ortho- and meta-silicic acids and their derivatives, the union between silica and base depends on the nature of the latter. There is reason for believing that the most easily decomposable are the simple silicates of the alkalis and alkaline earths, *i.e.* those compounds that are salts of strong bases and weak acids, or of weak acids and bases, and so undergo hydrolysis most easily. Observations on the weathering of ferromagnesian silicates frequently show that the first stage consists in the separation of an isomorphously admixed iron silicate which then breaks up with the formation of hydrated ferric oxide. (A change of this kind is the discoloration of black magnesian micas (biotite), olivine, etc.)[1]. On the other hand the union between silica and magnesium is extremely strong, which thus explains the large amount of vadose magnesium silicates. We shall return to this question later.

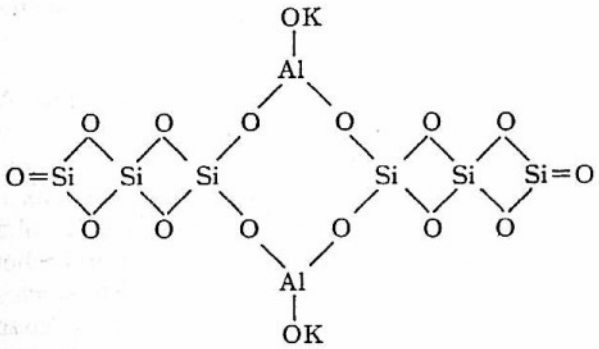
From the aluminosilicates of varied and complex structure (p. 79) silica separates under different conditions at varying rates depending on the position it occupies in the structure of the mineral. Thus, from one and the same compound part of the silica may separate comparatively easily, while another part occupying a different structural position only separates with difficulty. The most stable union is to be found in the so-called kaolin nucleus, which forms the basic structure of the bulk of the primary aluminosilicates (feldspars, micas, garnets, etc.).[2] This nucleus has a ring structure as represented by the following structural formula showing the simplest acid of this type :—

[1] This phenomenon is complicated by reactions of colloidal synthesis which will be discussed below.

[2] See p. 210.



It is seen that silica is here strongly bound to aluminium through oxygen. The silicon in other compounds containing this nucleus is of a somewhat different nature, *e.g.* orthoclase :—



In this case, in addition to the silicon of the kaolin ring bound strongly to alumina, there is the silicon of the side chains united only to oxygen and therefore easily separated as silica during the decomposition of the mineral.

The kaolin nucleus can only be broken under laboratory conditions by the use of strong reagents (*e.g.* boiling with sulphuric acid). This fact and the occurrence of many secondary, including vadose, minerals which still retain this nucleus in their structure is sufficient reason for believing that it is exceptionally stable under the conditions of the crust of weathering. Actually this stability is only relative. It has now been shown experimentally and confirmed by

field observations that certain organisms (diatoms) can break the kaolin ring and utilize the silica in the *construction of their shells*.[1] The nucleus is apparently broken up by natural acids independently of the activity of organisms, although the process is naturally much slower than in the laboratory. This is especially marked where desulphofication alternating with oxidation results in the formation of sulphuric acid.[2] Many analyses of soils and of the products of weathering of rocks and minerals, and experiments on artificial weathering have shown that alumina is more soluble than would be expected in compounds with the unbroken ring. It may be taken that the stability of the kaolin nucleus in soils and in the crust of weathering has been somewhat over-emphasized. We shall return to this question later. In connexion with aluminosilicates with a different structure the question of an especially strong union between Si and Al has apparently not arisen (p. 78).

### 2. Silica Gels and Their Crystallization. The Absorption of Silica by Organisms

Dissolved silica, as we have seen, is of common occurrence throughout the crust of weathering, and its further changes are extremely varied; part falls out of solution as gel or coagel, and a considerable part is used up by both land and marine organisms. The form in which silica is precipitated from solution depends on a variety of conditions. From concentrated solution it settles in large jelly-like flocs; in other circumstances it precipitates in flocs of varying sizes, which on drying form a powdery mass. In certain cases (*e.g.* the action of alkali sulphates on the sol) it falls out of solution as a hard precipitate which has a crystalline appearance but which does not react to polarized light.[3] It is apparently possible to find examples of all these types in nature. During the construction of the Simplon tunnel a

[1] Recent experiments by V. I. Vernadsky *et al.*, and by Kupen, have shown that the diatoms coexist with bacteria, and which of these actually decompose the nucleus cannot be accurately ascertained. *Cf.* V. I. Vernadsky, Geochemie, S. 132 (Leipzig, 1931).

[2] *Cf.* B. Polynov and P. Martinov, "The influence of desulphofication on soils," *Ann. Sect. Hydrotech.*, etc., Leningrad, Pt. XXIII, 1931.

[3] Observation of Prof. Akatov.

moist gelatinous mass of silica containing little crystals of quartz was found in a crack in the gneiss some 300 metres from the Italian side.[1] Similar occurrences of "fresh" silica gel which is easily cut with a knife have been noted elsewhere: Rezhbania, Chervenitza in Hungary, Champline (Dept. Seine) in France, etc. Much commoner are the solid masses of silica gel, known to mineralogists as *opals* (hyalite, precious opal, hydrophane, menilite, etc.). The forms in which these occur (films covering stones, masses occupying cavities and cracks in rocks and wood) clearly indicate their origin. One of these minerals (hyalite) occurs in a state of great purity, consisting simply of hydrated silica ($SiO_2.nH_2O$); others are contaminated with various bases and sesquioxides. *It is very important to note that magnesium is the base that occurs most frequently.* Magnesium opals form a special group of menilites, some of which contain up to 10% MgO. In the same way special groups of aluminium and iron opals are distinguished; in these the sum of sesquioxides may exceed 10%.

Such types of opals are usually explained by the mineralogist as due to "accidental contamination," whereas their formation offers nothing unusual and follows naturally from the colloidal properties of silica. We have already mentioned that in the crust of weathering silica sols are negatively charged and consequently are able to adsorb cations from solution and, at a certain stage in the adsorption, to coagulate. This adsorptive power is also retained up to a point by the gel which is in contact with a solution. The origin of the bases in opals is thus obvious. Silica sol may be coagulated without the adsorption of metallic cations, *e.g.* in acid solution, by the adsorption of hydrogen, and so the occurrence of the pure opals (hyalite) becomes understandable. Recent experiments have shown that adsorbed magnesium is comparatively easily replaced, but the wide distribution of magnesium opals suggests that once the sols and gels have aged the magnesium is most difficult to remove. Finally, it has been shown that the protective action

[1] In this case, nevertheless, the original solution can hardly be considered vadose.

of silica on sesquioxide sols obtains only when these are together in definite proportions. When this ratio reaches a certain value the sols discharge each other and form a complex coagel. This explains the varying amounts of sesquioxides found in opals, for the coagulation value is bound to vary with different solutions.[1]

Opal, the solidified gel with an indefinite water content, is a typical example of a transition form of a vadose mineral. It slowly loses its water and passes into a crystalline state, chalcedony, which so often shows its origin in its external form,[2] and secondary quartz. The latter is as stable in the crust of weathering as the primary variety.

The crystallization of natural mineral gels and consequently the presence in the deeper parts of the zone of weathering of crystalline analogues of the colloids characteristic of the surface were long ago noted by Cornu,[3] who showed their importance. The clearest demonstration of such changes is provided by the simplest compounds (opal—secondary quartz, colloidal alumina—hydrargillite, hydrotroilite—marcasite, etc.). With more complex coagels and adsorption systems the change is not quite so simple. In the system silica—adsorbed cation there can be no simple stoichiometric relation between the adsorbent and the adsorbed cation, for it is only the surface molecules of the micelle that take part in the reaction. It is evident that such a system could not possibly change into a single crystalline individual. It can crystallize, however, forming either aggregates of several stoichiometric compounds or crystalline bodies of a more complicated structure such as isomorphous mixtures and solid solutions. In particular it has been shown that a partial change of magnesium opals into magnesium silicates of the *sepiolite* type is possible.[4] Similar

[1] These explanations cannot, of course, be applied to all varieties of opal and chalcedony that contain an admixture of sesquioxides or other metals. An increase in the concentration of a complex solution, *e.g.* by simple evaporation, will result in the formation of the greatest variety of mixtures.

[2] Of special interest in this connexion are varieties of chalcedony known as agates, whose structure was explained by a study of the phenomena of the diffusion of solutions in gels. *Cf.* Liesegang, *Koll. Zeit.*, 1907-08, and Geologische Diffusionen, Dresden, 1913.

[3] *Cf. Kolloid Zeitschrift*, 1909, Bd. IV, H, 6.

[4] A. Damour, *Bull. Soc. Min.*, 1889, 7. *Cf.* G. Migeon, *ibid.* 1937, **59**, 6-134.

assumptions may be made in connexion with the coagels of silica and sesquioxides, but we shall return to this question later.

It may be felt from the above description of the properties of silica gels and opals that we are dealing with minerals which, like many described by mineralogists, are comparatively rare for the crust of weathering, are only of local occurrence, and being somewhat rare are stored away in museums, not being characteristic of the general processes peculiar to the crust of weathering. Such a conclusion, however, would be quite erroneous. Opals were used as an illustration simply because they demonstrate so graphically processes that are both *widely diffused in, and typical of,* the zone of weathering. In addition to these well-formed minerals there occur innumerable formations of varying size, not of local occurrence, but widely distributed throughout that zone. This could hardly be otherwise, and further examples could easily be given. Silica occurs in all vadose waters and in the solutions percolating through clastic deposits and sediments. In the latter it frequently separates out in large quantities as a gel ($SiO_2.nH_2O$) and forms a cement for such rocks. Quartz sands are thus converted into quartzose sandstones in which quartz grains are bound together by the secondary variety formed as a result of the crystallization of the silica gel. A similar kind of cementation is occasionally encountered in other clastic deposits and even in organic residues (*e.g.* petrified wood). These facts make the rôle of vadose silica quite clear. It is obvious that its forms are not only unconnected with any definite locality, but are frequently important members of the rock-forming minerals. The minerals to be described later are of equal importance.

The precipitation of silica gel from solution and the formation of solid opals is the first phase in the transition of silica into that inert form, *i.e.* secondary quartz, in which it leaves the crust of weathering.

Of much greater variety is the fate of the silica which is absorbed by organisms either from solution or directly from silicates. It is absorbed by higher plants from the soil solu-

tion and may form quite a considerable proportion of the mineral content. In certain groups of plants it reaches 3-4% of the dry matter and more than 40% of the weight of ash. Liebig was the first to subdivide plants into groups: (1) potassic, (2) calcareous, (3) siliceous, according to the content of each of the three elements. In the last group were included the cereals, the straw of which shows an especially high silica content (barley 17·27-36·73%; oats 33·46-55·95%[1]). The exact rôle of silica in plant growth is still not clear. It is generally assumed that it plays only a secondary part, such as the protection of the plant against parasites by the silicification of the cellulose sheath of the epidermis, or the increasing of the rigidity of the stem. Recently, however, its importance in more complex biological processes has been shown. It now appears that silica is an important factor in the utilization of phosphoric acid by plants. Hall and Morison showed an increased assimilation of $P_2O_5$ in the presence of silica; Schollenberger and Shedd pointed out the stimulating effect of silica on $P_2O_5$-deficient soils, and finally Lemmerman and Wiesman showed that silica may replace phosphoric acid to some extent.[2] Still more recently it has been shown that silica takes part in the formation of starch. No small part is played by silica in the animal organism, where it is apparently found not only in the outer covering but, as in plants, may occur in the living plasma of the cells. There is no doubt that silica is of much greater importance in the living organism than is at present realized, and its exclusion from the group of organogens is not altogether correct.

Apart from the absorption of silica by plant roots, a considerable amount is taken up by the lower plants and animal organisms for the construction of their siliceous skeletons. In the same way as for carbonates we find that the silica content of sea-water is much lower than that of rivers, *i.e.* it has likewise been absorbed by organisms. While in river water the silica content may be from 10-50% of the total dissolved matter, its content in ocean and sea-

[1] Quoted from J. W. Mellor, Treatise on Inorganic Chemistry, VI, p. 142 (1927).

[2] J. W. Mellor, *loc. cit.*

water does not exceed a few hundredth parts of the dissolved matter.[1] The organisms utilizing silica belong mainly to the diatom families, but include the siliceous radiolaria, and animals of the *Cœlenterata* groups (siliceous sponges). The siliceous muds formed by these organisms at the present time cover great areas of the Antarctic Ocean and the northern (sub-polar) parts of the Pacific Ocean. But this type of silica *organization,* in which it goes to the formation of shells and skeletons, is also found on land where it is carried out predominantly by diatoms. These are adapted to life under various conditions and in addition to occurring in water basins of the lake type, they are widespread in small periodic accumulations of water. Recently soil workers have been collecting more and more information on the rôle of diatoms in the formation of solods and even of podzolized soils.[2] Historico-geological relics of accumulations of diatomaceous material are found in sedimentary and metamorphic rocks: infusorial earth, certain quartzites and jaspers. Infusorial earth consists of an accumulation of unaltered or little altered diatom skeletons, and certain quartzites, jaspers, etc., are the crystallization products of accumulations of siliceous skeletons. This change takes place according to the scheme with which we are already familiar: opal—chalcedony—quartz.

In this way, silica takes an active part in the transformations occurring in living matter,[3] in which it assumes forms as yet unfamiliar to us. On leaving the living organism it enters the deeper zones of the earth and there passes through opals into secondary quartz, *i.e.* passes from the cycle of the sphere of weathering into the greater cycle of the earth's crust.

[1] F. W. Clarke, The Data of Geochemistry, 5th ed., 1920, p. 127.

[2] Solod is a soil that has developed from saline soil by the natural desalinization of the latter. Large numbers of diatoms were found in solodized soils near Lake Gokeha (Armenia) collected by A. A. Zavalishin. Their presence in many other cases has been shown by Prof. I. V. Tiurin, who suggests that they take an active part in the process of solodization itself. In addition, diatoms have been found in podzols from the Kola peninsula.

[3] According to V. I. Vernadsky, the amount of silica combined in organisms reaches several thousand million metric tons. It is obvious that the amount *passing through* organisms must be immeasurably greater. (See Geochemie, S. 129.)

### 3. Juvenile Forms of Aluminium. Aluminosilicates and Their Structure

The account we have just given of the changes undergone by silica in the crust of weathering has not touched at all on those vadose forms in which it is associated with alumina. This omission was intentional since the aluminosilicates are more easily described in connexion with the story of aluminium.

The juvenile forms of alumina are of great variety, the principal one being the unhydrated form already mentioned—corundum and its coloured varieties. The series of aluminates consists predominantly of magnesium salts ($MgAl_2O_4$) occurring in isomorphous mixture with those of iron, manganese and zinc (spinel), and more rarely aluminates of beryllium (chrysoberyl). Finally, there is the vast group of aluminosilicates. Of juvenile, or at any rate of primary origin for the crust of weathering, there are certain aluminium sulphates (*e.g.* the ammonium alum of the Etna crater, the solfataras near Pozzuole, and the alums common in many lavas); and a group of halogen compounds consisting mainly of fairly rare minerals: cryolite $Na_3AlF_6$, fluellite $AlF_3.H_2O$, prosopite $2Al(F,OH)_3.Ca(F,OH)_2$, pachnolite $AlF_3.NaCaF_3.H_2O$, etc. The non-oxygen compounds of aluminium are confined solely to this last group of rare minerals which cannot play any great part in the aluminium cycle. These compounds are unstable in the crust of weathering and are readily converted into oxygen compounds of aluminium.

The juvenile oxides of the corundum group are extremely stable, but there are indications that the hydration of corundum in the crust of weathering is possible. This results in the formation of hydrated alumina (diaspore).[1] On the other hand, corundum is commonly present with primary quartz among the residual products of weathering (sands from the disintegration of primary rocks). The minerals of the spinel group are also fairly stable; they are usually resistant to acids and alkalis, and are not infre-

[1] J. Roth, Allgemeine und chemische Geologie, Bd. I, S. 230 (Berlin, 1879).

quently also present among the residual products of weathering. Among the very few reports of the weathering of spinels we find descriptions of their transformation into the so-called houghite, hydrotalcite and volknerite. These apparently consist of mixtures of hydrated alumina with magnesium carbonates and form pseudomorphs after spinel.[1] The change may be represented by the equation :—

$$MgAl_2O_4 + CO_2 + H_2O = MgCO_3 + Al_2O_3.H_2O.$$

There are thus numerous sources for the hydrated alumina of the crust of weathering; nevertheless compared with aluminosilicates they represent only a small proportion of alumina compounds.

These aluminosilicates yield so great a variety of vadose products in addition to hydrated alumina that the character of the products can only be fully appreciated if the nature of their sources is fully understood. The structure of the aluminosilicates in spite of a great many investigations is still one of the most complex problems in mineralogy. This is not the place in which to give a detailed account of all the theories advanced for the chemical structure of these minerals, and we can only bring forward a few, yet important, points from the investigations on this problem. The first and most significant achievement was the theory of *aluminosilicic acids* (Vernadsky) on which a number of hypotheses may be based, including that in which aluminium plays the part of a base in the structure of the minerals. Certain investigators still do not agree with these views, but objective data show that this hypothesis must receive wide acceptance because the majority of the changes undergone by the aluminosilicates and various phenomena observed during laboratory investigations of the minerals can only be explained by this theory. The theories of P. Groth and Berzelius can no longer be accepted. The many other conceptions of the structure of aluminosilicates may be said merely to represent definite phases in the development of the

[1] *Ibid.*, Bd. I, S. 223. P. Groth, Tabellarische Uebersicht der Mineralien, Braunschweig, 1898, S. 172. C. F. Naumann, F. Zirkel, Elemente der Mineralogie, Leipzig, 1907, S. 507.

theory that has been most fully worked out by Vernadsky.[1] According to the latter the majority of the aluminosilicates may be divided into four groups depending on their chemical structure. To the first belong those compounds that have the kaolin ring as the basis of their structure.[2] This group includes the majority of the minerals. These minerals may be either simple salts or isomorphous mixtures of salts of aluminosilicic acids, $H_2Al_2Si_{2n}O_{4n+4}$, *e.g.* the feldspars :—

$CaAl_2Si_2O_8$—anorthite,
$K_2Al_2Si_6O_{16}$—orthoclase,
$Na_2Al_2Si_6O_{16}$—albite,

or more complex compounds such as the so-called *addition compounds, e.g.* the garnets :—

$MgAl_2Si_2O_8.Mg_2SiO_4$—pyrope,
$FeAl_2Si_2O_8.Fe_2SiO_4$—almandite,
$MnAl_2Si_2O_8.Mn_2SiO_4$—spessartite,
$CaFe_2Si_2O_8.Ca_2SiO_4$—andradite, etc.

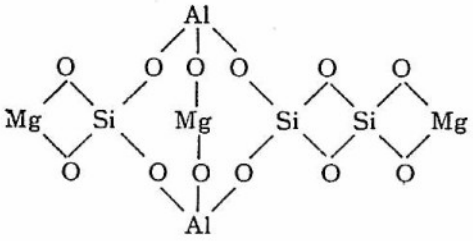
The general formula of these products of the addition to aluminosilicates of the kaolin nucleus may be expressed in the following form :—

$$pR^{II}Al_2Si_{2n}O_{4n+4}.qA,$$

where A represents the group of elements that is added to the kaolin nucleus (in the case of the garnets $R^{II}_2SiO_4$). The value of p in the formula is variable, 1, 2, 3, 4, etc., but q is always 1 or 2. The most important characteristic of these additive compounds is that *their general properties are independent of the composition of group A, and retain a close connexion with the properties of the nucleus.* It is thus apparent that garnets do not share the properties of the orthosilicates, although the added group is orthosilicic in nature. On the other hand the properties of salts of aluminosilicic acids are expressed very clearly in garnets corresponding to the structural formula (pyrope) :—

[1] C. Doelther, Konstitution der Silikate, *Handbuch der Mineralchemie*, 1914, Bd. II, S. 61-69. *Zeit. Kryst.*, 1901, vol. 34. *Ann. Acad. Sci.*, 1909, pt. 3 (Russ.).

[2] Certain authors have given alternative structures for this nucleus. *Cf.* H. Stremme in Fortschritte der Min. Kryst. und Petrographie, 1912, 2, 87-128. J. V. Samoilov, *Ann. Acad. Sci.* (Russ.), 1914.




This circumstance apparently allows both the simple salts of aluminosilicic acids containing the kaolin nucleus and the more complex additive compounds of the above type to be combined in one group.

An important property of this group is the formation of kaolinite ($H_2Al_2Si_2O_8$) as a result of the transformation of the members. This may be regarded simply as the usual change of a salt into an acid, but of that we shall have more to say later.

The second group of aluminosilicates, which includes only a few minerals of the *melilite* and *ilvaite* type, has quite different properties, but these become clear on a fuller understanding of the chemical structure of the members.

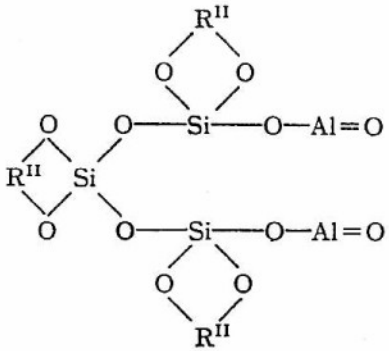
Suppose that we have a mineral with a chemical composition absolutely identical with that of garnet, but in whose structure there has occurred a transposition, viz., the group A which was added to the aluminosilicate nucleus of the garnet has now become the basic nucleus, the ring system of the garnet playing the part of the additive group.[1] The difference between it and the garnet may be expressed by the following formulæ :—

| $R^{II}Al_2Si_2O_8.R^{II}{}_2SiO_4$ | $R^{II}{}_2SiO_4.R^{II}Al_2Si_2O_8$ |
|---|---|
| Garnet | Isomer of garnet |

Following on what we have said, it is obvious that the properties of the isomer cannot be the same as those of the garnet, for they are determined by the orthosilicate nucleus, $R_2SiO_4$. The properties of the aluminosilicate salt of the kaolin nucleus are absent from the isomer, and its structural

[1] This type is described by Vernadsky as a transposition isomer, *Ann. Acad. Sci.* (Russ.), 1909.

formula does not retain the ring structure of the kaolin nucleus. The formula may be written :—

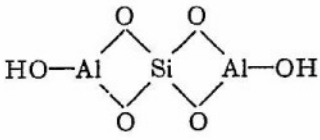


The minerals of the melilite and ilvaite group, although perhaps not pure isomers of the garnets, are at least very closely related to them :—

$3Ca_2SiO_4.(Ca,Mg)(Al,Fe)_2Si_2O_8$—melilite,
$Ca_2SiO_4.CaAl_2SiO_6$—gehlenite,
$2FeSiO_4.CaFe_2Si_2O_8.H_2O$—ilvaite, etc.

Corresponding to such a structure it is found that these minerals are much more easily decomposed by acids, are not so hard and, what is most important from our point of view, *they do not give aluminosilicic acids of the kaolin type on alteration.*

The minerals of this group include juvenile forms, a certain number of phreatic (*e.g.* secondary micas) and a still smaller number of vadose minerals. But in addition to these there is a considerable number of aluminosilicates of predominantly phreatic origin. These, according to their chemical structure fall into two groups: *chlorites* and *chloritoids*. One group consists of compounds that are neutral and acid salts of a specific aluminosilicic acid—*margaritic* acid ($H_2Al_2SiO_6$), with the following structure :—



To this third group of aluminosilicates belongs margarite, $CaH_2(Al_2SiO_6)_2$, which is an acid calcium salt of the above acid, and a small number of other minerals. The latter are mainly isomorphous mixtures of magnesium, calcium and manganese salts, the first predominating, and the addition products of the margarite nucleus (xanthophyllite, brandisite, ottragite).

Much more numerous are the minerals of the fourth and last group, which consists largely of magnesium aluminosilicates. Several of these minerals are noticeable constituents of certain metamorphic rocks (*e.g.* clinochlore, penninite, in the so-called chlorite schists). All the minerals of the group have an extremely complex structure, as can be seen from their empirical formulæ. They have not been much studied and their structure is not very clear. V. I. Vernadsky considers the chlorites to be salts, and isomorphous mixtures of salts, of polybasic aluminosilicic acids corresponding to the anhydrides, $Al_6Si_2O_7$, $Al_9Si_4O_{11}$, etc. We have the corresponding series of acids:—

$Al_2Si_2O_6(OH)_2$, $Al_2Si_2O_5(OH)_4$ . . . $Al_2Si_2(OH)_{14}$,
$Al_2Si_4O_{10}(OH)_2$, $Al_2Si_4O_9(OH)_4$ . . . $Al_2Si_4(OH)_{22}$.

In this group there are also the salts of analogous aluminosilicic acids (so-called thuringite). The most important property of the chlorites and chloritoids, as far as we are concerned, is that they are easily decomposed by acids, and during their decomposition in the crust of weathering give neither kaolinite nor any other product with an analogous structure.

### 4. The Formation of Aluminosilicate Adsorption Systems. Residual Aluminosilicic Acids

Let us now return to those minerals which form the first of our four groups, viz., to the aluminosilicates having the kaolin nucleus as the basis of their chemical structure. This group includes the majority of juvenile silicates and forms the main supply of aluminosilicic compounds in the crust of weathering. The gradual comminution of these minerals increases their specific surface and also the activity of that

surface. The final result is that the hygroscopic moisture originally adsorbed on the surface enters into closer and closer union with the surface molecules and the mineral becomes hydrated. Such phenomena have been studied experimentally with a number of aluminosilicates (feldspars, micas, augites, etc.). The water adsorbed in this way cannot exist in definite and constant molecular ratio with the primary mineral, for not all of its molecules take part in the adsorption at the same time. The water corresponds to that adsorbed by gels. This process is the first stage in the decomposition of the mineral, which now begins to assume certain colloidal properties, although it may yet retain its crystalline structure for some time.[1] We may assume that in the hydrated surface layer of the mineral there takes place a reaction similar to that characteristic of colloidal micelles, *i.e.* the dissociation of molecules and a definite distribution of the dissociated ions. If our mineral is a neutral salt, *e.g.* $R_2Al_2Si_2O_8$, the reaction taking place in the hydrated layer may be represented by the equation :—

$$R_2Al_2Si_2O_8 + H_2O \rightarrow 2R' + 2OH' + \text{col. } Al_2Si_2O_7,$$

and the structure of the molecules may be represented by the scheme we have already used :—

$$[Al_2Si_2O_7 \ . \ . \ . \ nOH']nR'.$$

In this way the metallic cation, formerly the base of the salt, passes into the adsorbed state, and may be removed and replaced by another cation. It is thus apparent that if we act on this sheath of the mineral with carbon dioxide, as happens in nature, we shall obtain the following system :—

$$[Al_2Si_2O_7 \ . \ . \ . \ nOH']nH'.$$

Since the inner portion of the mineral remains unchanged, its composition as a whole at any stage of the alteration will approximate to that of the acid salt :—

$$KHAl_2Si_2O_8.$$

As a result of this there arose the idea that acid aluminosilicates were the first stage in the breakdown of the minerals

[1] There is no contradiction in this statement since it has long been known that colloidal properties are not acquired on attaining a certain particle size, but are developed gradually and are apparent to some extent even in coarse suspensions.

of the first group during weathering. Actually, however, both laboratory experiments on the action of water with and without carbon dioxide on minerals, and field observations have shown that we are not dealing with the usual simple interaction of acid and salt. This assumption would not satisfactorily explain numerous phenomena. The reactions are typically surface phenomena and occur at the solid-liquid interface, being to a great extent characteristic of the colloidal state.[1] The beginning of the change is manifested outwardly in the clouding of the surface of the mineral. Loewinson-Lessing has referred to this change as it occurs in feldspars as *pelitization*. This clouding is due in the main to the fact that many of the products of the reaction between the liberated exchangeable cations and carbon dioxide ($R_2CO_3$), as well as other substances physically adsorbed together with water, are precipitated on the surface of the mineral.[2] But under definite conditions the change we have described may take place without the destruction of the crystal structure of the mineral. There is nothing unexpected in this if we remember that many highly disperse systems show a crystalline structure. The isotropy of colloidal systems, and especially of gels, can be explained by the irregular distribution of the micelles, but the disposition of the molecules *within the micelles* may still conform to the crystal structure of the mineral. In such cases, therefore, in which the crystal is not mechanically disintegrated, the reacting solution covers it with a film and slowly, as the surface molecules alter, penetrates deeper without disturbing the positions of the molecules (intramolecular penetration), thus changing the composition without affecting the crystal structure of the mineral. The optical properties, however, can hardly remain unchanged (refractive index, double refraction, etc.). Such products of the weathering of aluminosilicates (feldspars, micas, augites) were described by K. D. Glinka, and in some cases the change had taken place throughout the entire mineral, which was practically free from bases, *i.e.* it

[1] The ability of finely powdered feldspar to exchange its bases with a solution in contact with it has been shown in an experiment carried out at my request by P. N. Stephanov (results unpublished).

[2] A. Gabriel, *loc. cit.*

had been converted into an aluminosilicic acid.[1] Such cases are, however, comparatively rare. The usual products of weathering undergo mechanical comminution, become thoroughly intermixed, have an amorphous appearance and are extremely difficult to separate mechanically. Nevertheless, as a result of the study of the properties of individual minerals and of work similar to that of Glinka, we can now state that aluminosilicates with a kaolin nucleus give rise to secondary aluminosilicates of the following types:—

I. A system which still retains a residuum of undecomposed mineral, and may be represented thus:—

$$[SiAlR \ldots SiAl \ldots nOH']nH',$$

where SiAlR represents the undecomposed portion without adsorbed water, and to the right within the brackets we have the system of dissociated molecules with a sheath of hydroxyl ions, which determine the sign of the charge; outside the brackets we have the swarm of adsorbed ions. As weathering proceeds these ions will be largely hydrions, but under definite conditions (composition of the reacting solution) metallic cations may play a greater or less part.

II. Aluminosilicic acids in the colloidal state:—

$$[SiAl \ldots nOH']nH';$$

in other words, a system in which the primary mineral has undergone a complete change, while still retaining for a time the original crystal structure; it is, however, essentially amorpho-colloidal. The ability of such systems to be dispersed, to give sols, and to adsorb cations, has been shown experimentally and confirmed by natural phenomena. It will be sufficiently accurate to assume the existence of two main types of weathering products:—

1. The weathering product of aluminosilicates of the type $R_2Al_2Si_2O_8$, *e.g.* colloidal kaolinite, $H_2Al_2Si_2O_8.nH_2O$.

2. The weathering product of aluminosilicates of the type $R_2Al_2Si_6O_{16}$, e.g. colloidal termierite, $H_2Al_2Si_6O_{16}.nH_2O$. We may also assume that the second can pass into the first.

[1] K. D. Glinka, Investigations on weathering processes (Russ.), 1906.

Like the gels of silica these colloidal substances can under suitable conditions give rise to crystalline varieties :—

$H_2Al_2Si_2O_8.H_2O$—crystalline kaolinite, and
$H_2Al_2Si_6O_{16}.6H_2O$—crystalline termierite.

The existence of the crystalline acid *pyrophyllite*, $H_2Al_2Si_4O_{12}$, indicates the possibility of the colloidal variety, $H_2Al_2Si_4O_{12}.nH_2O$.[1] As we shall see later, there may be among the products of weathering aluminosilicic systems of an acidic nature but of another origin. In distinction to the latter, we shall apply Stremme's term *residual* to the group of colloidal aluminosilicic acids that retain the kaolin nucleus.

III. Products resulting from the adsorption of metallic cations by the residual aluminosilicic acids :—

$$[SiAl \ldots 2nOH']nR''(2nR'),$$

*i.e.* systems in which the adsorbed hydrogen is replaced by metallic cations. These systems are inevitable in the presence of the respective solutions.

The process of weathering just described, although in a somewhat different sense, is occasionally called *kaolinization*. Several investigators have objected to such an identification of weathering with kaolinization, pointing out that the properties of many kaolin-localities preclude its formation as a result of weathering. Without entering into the details of this " kaolin " dispute, which was at first of undoubted interest, but is now to a great extent unprofitable, we may give a few explanatory notes. Like many other compounds kaolin may be formed in various ways. The volcanic discharge of sodium chloride, sometimes in dense clouds, does not prevent the wide occurrence of rock salt. In the same way the

[1] Minerals corresponding in composition and structure to the aluminosilicic acids of the kaolin type are frequently referred to as *clays*. At the same time the term is also applied to a particular type of rock that may contain no clay mineral. The investigations of P. A. Zemiachensky have shown that the conception of clay (rock) may be related to a definite composition. There is thus a certain inconvenience in the use of the term *clay*. In the present work we have as far as possible avoided the use of the word in referring to minerals, and since the " clay minerals " usually have their special names and the whole group can be called a group of the kaolin type, this avoidance does not require the coining of a new term.

very energetic action of volcanic $CO_2$, hot springs, acid vapours, may, under definite conditions, give rise to kaolinization much more quickly than atmospheric weathering. There is therefore no reason for making kaolinization by weathering distinct from hydrothermal kaolinization. The very valuable data collected by Rösslet on the sources of kaolin and their interpretation are, of course, still valid, for it is difficult to imagine the formation by weathering of large amounts of kaolin in any one place. Weathering is a process of wide regional distribution, in which kaolinization is only a single phase, and the products of which are always complex and difficult to separate (Chap. V). The evidence that the products of weathering are colloidal, whilst those of pneumatolytic or hydrothermal action are not, is, of course, not to be doubted, but we must not forget that this distinction may be levelled out. Colloids may still have a crystalline structure, and crystalline kaolin may *weather* and pass into the colloidal state, still more easily since it already possesses many of the properties characteristic of colloids even in the crystalline state (*e.g.* the phenomena of adsorption in Carlsbad kaolin).[1]

### 5. The Disruption of the Aluminosilicate Nucleus

Numerous experiments have shown that kaolin is easily peptized to give a stable suspension under various conditions that are found in nature (the action of alkalis, of humic matter). It has also been shown that the electrical charge of the colloid may be reversed in an acid solution. This necessitates the breaking up of the kaolin ring (Mattson), and we are forced to admit the possibility of this happening during weathering and without the interference of organisms. In the presence of the latter we have already seen that this destruction of the ring has been definitely proved with resultant formation of free hydrated alumina and silica. The separation of hydrated alumina during the weathering of other minerals has already been mentioned (p. 78). We must

[1] In all these cases we understand by *crystalline state* the optical anisotrophy of the material for it appears necessary to recognize that all colloidal substances are crystalline.

therefore take into account this vadose form of aluminium compound.

The alumina content of natural solutions (river, spring and lake water) is in sharp contrast to that of silica, rarely exceeding 1% of the total dissolved matter. Nevertheless, it is almost invariably present, for the most part, as a sol, because the somewhat acid conditions necessary for its occurrence in a molecular-disperse state are usually absent in natural waters.[1] Under definite conditions (weakly acid solution) silica and humus sols may exercise a protective influence on colloidal alumina within certain limits of concentration and definite degrees of dispersion. The presence of aluminium in the composition of organisms indicates the wide distribution of its solutions. Sols of alumina, however, as was shown by Graham, are extremely unstable systems. Even hydrosols containing not more than 0·5% $Al_2O_3$, for example, turn into gels after standing for a few days. It may be remarked here that this power of mineral colloids to change their state of aggregation and their properties with lapse of time, even when the conditions in the medium remain more or less unaltered, plays an important part in the crust of weathering. Although the amount of alumina in natural waters is small, it is constant, and although both its true and colloidal solutions are unstable, we nevertheless have reason to believe that a considerable quantity of alumina passes through the sol state and that this state plays an important part in the cycle of changes undergone by aluminium compounds.

From natural solutions alumina separates either as a more or less pure gel, $Al_2O_3.nH_2O$, or more often in complex coagels with humus, silica, hydrated iron oxide and other systems. After some time alumina gels crystallize to form *hydrargillite*, $Al_2O_3.3H_2O$, or the less hydrated *diaspore*, $Al_2O_3.H_2O$.[2] Both the gels and the crystalline representa-

[1] Soil solutions of such an acidity (pH < 5) are, of course, common, and it is possible that alkaline solutions in which the aluminium would form an anion ($AlO_2'$) may also be found in nature.

[2] The hydrated alumina with two molecules of water apparently does not occur naturally. Such a composition is often given to *bauxite*, but bauxite is not a mineral, but consists of a mixture of colloidal alumina with hydrated ferric oxide and allophanoids.

tives of the vadose forms of free alumina are comparatively rare minerals, and this has strengthened the view that the kaolin nucleus of aluminosilicates is extremely stable in the crust of weathering. Kaolinite and other derivatives of aluminosilicates were once regarded as the "end-products" of weathering and the disruption of the nucleus as an exceptional and rare occurrence. Actually the comparative rarity of the vadose forms of free alumina is due to the conditions under which its sols coagulate. The separation of the pure gel is apparently dependent on specific conditions (p. 74), and in the majority of cases the alumina forms coagels, for the most part with silica. There is reason to believe that in many of the reactions in the crust of weathering, alumina, in contrast to silica and kaolinite, behaves as a positively charged colloid, able to adsorb anions. It is quite possible that the vadose phosphates of alumina (wavellite, callainite, fischerite, peganite, variscite, etc.) are no less than crystallized adsorption systems of alumina with phosphoric acid.[1] In favour of this theory we have the following facts: these minerals have an indefinite composition in which the ratio $Al_2O_3 : P_2O_5$ varies widely; there is usually an excess of alumina, as would be expected of the adsorbent (*e.g.* certain wavellites have the composition $AlPO_4.2Al(OH)_3.6H_2O$); and, in addition, the frequently microcrystalline structure which is sometimes hardly visible, so characteristic of solidified gels, is a feature of callaite and many of the wavellites. The case of aluminium sulphates is, of course, a different matter, and many of these must be of vadose origin. Examples of the formation of vadose sulphuric acid have already been given (p. 36), and there is no doubt that its action on aluminosilicates and aluminates, and more so on the forms of free alumina, ought to result in the forma-

[1] It is a well-known fact that alumina, like iron oxide, is amphoteric in character, appearing in certain compounds as a base and others as the acid radical (*e.g.* spinel). This property is also retained in the colloidal state. Thus, in an acid medium the outer molecules of the alumina micelle are surrounded by a *hydroxyl sheath, i.e.* $[Al(OH)_2]^+.OH^-$, the hydroxyl ions being replaceable with $Cl'$, $HCO_3'$, $SO_4''$, etc. In an alkaline medium, hydrogen ions form the outer sheath $[AlO(OH)_2]^-.H^+$, and may be replaced by other cations. It should be noted that recent investigations have raised the question of the *ampholytic* nature of minerals colloids (Mattson, Antipov-Karataiev, Nikolsky).

tion of aluminium sulphate. Rare cases of the formation of these vadose forms of alumina and their adaptation to conditions in which oxidation alternates with reduction processes do not contradict the above explanation. The sulphates do not form stable systems in the crust of weathering: they represent only transitory forms of the vadose compounds of alumina and give up their sulphate ion to other cations, the alumina passing into another state. It appears that only a very small fraction of the alumina takes part in this phase of its cycle.

### 6. Aluminosilicic Coagels

An immeasurably greater rôle is played by the coagels of alumina, and the first place among these must be accorded to its colloidal compounds with silica. Experiments with artificial coagels of alumina and silica at first sight might seem unconvincing proof of similar processes in nature.[1] At least we find such statements in the literature and even in treatises of a general character. They are based on the small amounts of alumina and silica in natural solutions and on the small probability of these occurring together in any quantity.[2] It is not difficult to see that the error in such reasoning lies, first of all, in the application of laboratory standards to natural conditions. There is no doubt that from the viewpoint of laboratory experiment the amounts of silica and alumina occurring in natural waters are not of much account compared with those required to give a clear illustration of the processes at work. In nature time is limitless, and the minutest causes can give rise to immense effects as a result of the prolonged process. In addition, it must not be forgotten that there are various powerful, though transitory, reagents that occur in definite parts of the crust of weathering and play a very great part in the transformation of vadose minerals. Thus, it is well known that the solutions circulating in many soils are fairly strongly acid, while in other places the reaction may be just as alkaline. This highly acid or alkaline reaction *is*, of course, *not retained* as

1 Many such experiments have been carried out recently.
2 K. D. Glinka, Text-book of Soil Science, p. 178 (4th ed., Moscow, 1931).

the solutions percolate downwards. At any given moment only a small amount of the solution circulating in the upper part of the soil reacts with the mineral matter, but in course of time the products of this action may reach a considerable magnitude. This is exactly what happens in the case of silica and alumina.

It may be asserted that the sols of alumina and silica, notwithstanding Glinka's view, are encountered in practically all solutions in the crust of weathering, as is indicated by the numerous analyses of river, lake and other natural waters. If we calculate the mean ratio of silica to alumina in river waters we obtain a figure of about 50 or even more. In individual instances the ratio fluctuates widely, as is shown by the following values selected at random :—

| | $SiO_2 : Al_2O_3$ (Weight) | $SiO_2 : Al_2O_3$ (Mol.) |
|---|---|---|
| River Columbia (N. America) | 300 | 490 |
| River Iltza (Danube basin) ... | 4 | 6·7 |
| River Iser (near Munich) ... | 1·45 | 2·4 |

As regards the absolute contents of these hydrated oxides in river water, the value of silica does not as a rule exceed 0·001%. The contents in the soil solution are of another order. Water extracts of soils frequently remove up to 0·01% silica or more. It may be assumed that the more concentrated natural soil solution may contain, although for only a short time, a much greater amount of silica. Unfortunately there is not sufficient material available on the quantitative ratio of silica to alumina in water extracts from soils, but the following data give some idea of the results obtained[1] :—

| | $SiO_2 : Al_2O_3$ (Weight) | $SiO_2 : Al_2O_3$ (Mol.) |
|---|---|---|
| Solonetz from Saratov, horizon 1 | 1·5 | 2·5 |
| ,, 2 | 0·8 | 1·3 |
| ,, 3 | 1·7 | 2·9 |
| ,, 4 | 2·4 | 4·0 |
| ,, 5 | 0·8 | 1·3 |

[1] *Cf.* K. D. Glinka, Text-book of Soil Science, p. 452, 4th ed., 1931.

We see that the relative amount of alumina in the soil solution may be comparatively considerable. The data quoted refer to a soil solution of alkaline reaction. In the much more widespread solutions of acid reaction we may expect a much higher relative content of alumina. The available data show that not infrequently in water extracts the ratio of silica to the sum of sesquioxides reaches only 0·2. If we assume the alumina to amount to even one-third of the sum of sesquioxides, the ratio $SiO_2 : Al_2O_3$ is about 0·6, and the calculation of the molecular ratio does not raise the value to more than unity. Consideration of the sharp fluctuations in the contents of silica and alumina and electrolytes in natural vadose solutions including river and sea water, and the diverse conditions under which the mutual coagulation of oppositely charged colloids takes place, in particular that of silica with alumina, leads to the conclusion, *a priori*, that *coagels of alumina and silica ought inevitably to be formed and in some cases to accumulate in the crust of weathering.* Remembering the extreme instability of the more weakly dispersed colloids such as silica and alumina, and their very transitory existence, it must be concluded that the analyses of river and other natural waters can hardly give a true conception of the amounts of these compounds that pass through the sol state. Clear confirmation of this is to be found in numerous natural compounds which are by nature aluminosilicates with varying values of the ratio $SiO_2 : Al_2O_3$ and very definite colloidal properties, *e.g.* allophane, collyrite, schrötterite, etc. There appears to be no doubt that in such cases we are dealing with the products of colloidal synthesis, and mainly with coagels at varying stages in their further transformation.[1] This finds ample confirmation in the wide occurrence of ferri-silicic and ferri-alumino-silicic systems containing hydrated ferric oxide. The qualitative properties of the colloidal forms of hydrated ferric oxide resemble those of alumina in many ways, including that of mutual coagulation with silica.

[1] It should be remembered that the gel, in contrast to the sol, includes a series of states that follow after one another (dehydration, solidification) and usually conclude with crystallization. A gel is a dynamic system, which not only may react with outside reagents, but can undergo internal change (the "aging" of gels).

## 7. Allophanoids

Setting aside for a moment the ferrisilicic compounds, we shall call the siallite group resulting from colloidal synthesis *allophanoids* (after Stremme) in distinction to the group of *residual* aluminosilicic acids. Experiments and theoretical considerations admit the possibility of the real existence in the crust of weathering of both positive and negative colloidal synthetic aluminosilicate systems, *e.g.* $[SiAl \ldots nOH']nR^{\cdot}$ and $[SiAl \ldots nAl(OH)_2^{\cdot}]nX'(\frac{n}{2}X'', \frac{n}{3}X''')$, where X may be $Cl'$, $OH'$, $HCO_3'$, $SO_4''$, $PO_4'''$, etc. There is no doubt about the existence of the acid-like systems for there are sufficient examples in which such systems contain either adsorbed hydrogen or metallic cations —in the latter case they show a salt-like character. To this type belong, apparently, all cases in which the $SiO_2 : Al_2O_3$ ratio is not less than 2, and in which the excess of negative charges on the silica confers this charge on the whole system. The point at which such a sol coagulates seems to be independent of the quantitative ratio of silica to alumina, but is dependent on other natural factors (action of electrolytes, changes in concentration, temperature, etc.). Much more rarely do we encounter facts supporting the existence of electropositive colloidal siallites. Nevertheless they do occur. To this group can be referred certain allophanes with a $SiO_2 : Al_2O_3$ ratio of unity or less. In these it would seem that calcium bicarbonate is present in the adsorbed state. It is, of course, possible that one part of the allophane adsorbs the calcium ion and the other the bicarbonate ion.[1] In view of the occurrence of pure gels, $Al_2O_3.nH_2O$, definite transition stages from electro-negative to electropositive aluminosilicic systems may be assumed. Naturally the nearer the latter approaches a pure alumina gel the less common it will be since it is connected with the conditions under which colloidal alumina systems are formed and the small amount of pure alumina gels available.

Thus, among the active vadose forms of compounds of silica and alumina we ought to distinguish :—

[1] *Cf.* Samoilov and Cherviakov, " Allophane from Riazan and adsorption minerals," *Ann. Acad. Sci.* (Russ.) 1915.

(a) Allophanoids with an $SiO_2 : Al_2O_3$ ratio of 2 or more. These complexes we shall refer to the group of *siallite* vadose compounds;

(b) Allophanoids with a ratio of less than 2. To this group we shall apply Harrassowitz's term *allite-siallite*,[1] while admitting the possibility in certain cases of their colloidal forms being electropositive, and finally,

(c) The various alumina gels and their derivatives which we shall call *allites*.

Up to the present we have dealt exclusively with the products of the weathering of aluminosilicates of the first group, *i.e.* those containing a kaolin nucleus. There still remain three groups, which, although obviously of less account than the first, nevertheless play a part in the crust of weathering. In analogy to the first group, inasmuch as all these minerals are salts of aluminosilicic acids, it ought to be admitted that these latter can also give colloids of the corresponding acids among the *residual products*. But taking into account the weak union between silica and alumina in the structure of these acids, the unusual complexity of the molecules of certain members, and their generally low stability (*e.g.* to acids) it is correct to assume that weathering inevitably results in the breakdown of the aluminosilicate radical, or at the most its extremely transitory existence among the products of weathering. Previously we assumed the existence of a complex colloidal ion, $Al_2Si_2O_7$ as the dissociation product of the hydrated sheath of certain minerals, but this contained the stable ring nucleus, whereas it is absent from minerals of the mellilite, chloritoid and chlorite groups. The retention of their frequently complex and unstable radicals in a hydrated state is thus difficult to conceive. This difficulty is emphasized by the non-existence of vadose crystalline varieties of such acids as margaritic acid, etc., which do not belong to the group with the kaolin nucleus. It is probably correct to assume that the aluminosilicic products of the weathering of these minerals consist of the compounds of colloidal synthesis, or less regular mixtures of gels of silica

[1] H. Harrassowitz, "*Laterit.*" *Fortschr. Geol. Paleontologie*, Bd. 4, H. 14, 1926.

and alumina and their products. In other words, the weathering products must be likewise referred to the group of allophanoids, for a stricter subdivision of this group cannot be made on account of the lack of data and of insufficient knowledge of these mineral gels. In the meantime it can only be assumed that the union between silica and alumina in these systems is variable even within one and the same system. It may approximate to the union of simple stoichiometric compounds, or it may resemble a solid solution, or simply a mechanical mixture, but this union is new and not residual from the original minerals. There is no doubt that all these compounds can give rise to adsorption derivatives, which will be discussed later in connexion with the elements taking part in the composition of the adsorbed ions.[1] These adsorption systems are frequently the transition form from vadose aluminosilicates to the state in which they leave the crust of weathering and enter the deeper shells.

## 8. Juvenile Forms of Iron

The next element to be discussed is iron, compounds of which have already been encountered frequently. The primary forms in which iron appears in the zone of weathering are of much greater variety than those of aluminium, and the amphoteric nature of both these elements shows up much more clearly in iron. Among the juvenile forms there is first of all native iron; but a fair amount of this native iron should be ascribed to cosmic and not to juvenile origin. Not so long ago treatises on mineralogy considered all native iron as being of cosmic origin, and its minerals as originating in meteorites and cosmic dust. At the present time, however, it is considered that there are definite kinds of native iron that have crystallized out from a molten magma and are therefore common in many basic rocks (basalts, peridotites). The iron occurs as fine particles scattered throughout the rock, only rarely occurring in large isolated masses. An admixture of nickel is usually characteristic of

[1] One such derivative is evidently *montmorillonite*, which is formed as a result of the adsorption of Ca and Mg by the colloidal system and its subsequent crystallization.

both juvenile and cosmic iron, but the amount is not constant.

It is evident that native iron interacts with oxygen and water in the crust of weathering, being first of all converted into hydrated ferrous oxide. This stage may be more or less transitory, the final product being hydrated ferric oxide:—

$$Fe + O + H_2O = FeO.H_2O.$$
$$2Fe(OH)_2 + O = Fe_2O_3.H_2O + H_2O.$$

Actually the ferric oxide formed on weathering is in a colloidal state $Fe_2O_3.nH_2O$, and only after a time changes into the monohydrate, which with an excess of water yields compounds of the solid solution type.[1] It should be noted that the forms of native iron that are richer in nickel are distinguished by a much greater stability.

Next come the compounds of iron with sulphur, arsenic and antimony. Among these are the monosulphides *pyrrhotite* and *troilite* (FeS); isomorphous mixtures of iron sulphide with nickel and zinc sulphides; iron disulphide *pyrites* ($FeS_2$); isomorphous mixtures of sulphoarsenic compounds with nickel and cobalt; pure arsenious *iron-löllingite* ($FeAs_2$); the sulphoarsenious *arsenopyrites* (FeAsS), and, finally, a group of minerals which are sulpho-salts, *i.e.* salts of acids of the types: $Fe(SH)_3$, $FeS(SH)$, $Fe_2S(SH)_4$, and their derivatives. To this group belong the copper salts: *bornite* $Fe(CuS)_3$, *chalcopyrites* $FeS(CuS)$; the silver salt: *sternbergite* $Fe_2S_2(AgS)$, etc. Certain chlorides are also of juvenile origin: *molisite* $FeCl_3$, and *erythrosiderite* $FeCl_3.2KCl.H_2O$, both of which are characteristic of the acid fumaroles of active volcanoes. Among the diverse natural oxygen.compounds of iron there are also many juvenile (and phreatic) forms: *hæmatite* $Fe_2O_3$; a series of ferrites such as *magnesioferrite* $MgFe_2O_4$, *manganese spinel* $MnFe_2O_4$, *magnetite* $FeFe_2O_4$, in which part of the iron acts as a base and the rest enters the acidic radical; aluminates, tungstates

[1] *Cf.* p. 38. Also I. S. Kurnakov and E. J. Rodé, The Chemistry of natural hydrated ferric oxide, *Ann. Inst. Phys.-Chem. Anal. Acad. Sci., USSR.*, 1927, vol. 3, pt. 1 (Leningrad). H. B. Weiser, Inorganic Colloid Chemistry, Vol. II, The Colloidal Hydroxides. New York and London, 1935.

and titanates of iron such as *pleonaste* from the group of spinels $(Mg,Fe)Al_2O_4$. In this group iron may replace aluminium isomorphously. Other minerals are *ferberite* $FeWO_4$, *ilmenite* $FeTiO_3$, *titanomagnetite* $Fe(Fe,Ti)_2O_4$, and manganates such as *bixite* $FeMnO_3$. There are also many cases in which iron is isomorphously replaced by either aluminium or chromium in the acid radical and by magnesium in the basic portion, while manganese may be found in either part.

In the vast groups of juvenile and phreatic silicates and aluminosilicates iron also plays a dual rôle. In the magnesian silicates it almost constantly replaces some of the magnesium, and in the aluminosilicates it replaces aluminium. It frequently acts independently to form *ferrisilicates* analogous to the aluminosilicates. Among the strictly juvenile minerals it should be noted that ferrisilicates, and the isomorphous replacement of aluminium by iron in the acidic radicals of aluminosilicic acid, are comparatively rare. The common group of feldspars, for example, is practically devoid of iron,[1] *but in the groups of phreatic minerals it is much more common.*

## 9. Vadose Forms of Iron

Turning now to the changes undergone by these compounds of iron in the crust of weathering and the formation of vadose minerals, it must be stated first of all that the *hydrated ferric oxide* already described is of very great importance. Ultimately it is the result of so-called "normal" weathering, *i.e.* the action of water, oxygen and carbon dioxide on all the above-mentioned compounds. Its high state of oxidation and hydration, and its wide distribution in the crust of weathering, have been the reasons for believing it to be an end-product, and in *equilibrium* with the thermodynamic conditions of the crust of weathering. It would be more correct, however, not to speak of equilibrium, but to regard hydrated ferric oxide as the *active form* of iron typical

[1] The iron feldspar investigated by Lakur and Beliankin is at least an extremely rare occurrence. *Cf. Ann. Acad. Sci., USSR,* 1926, pp. 1199-1206.

of the crust of weathering and an almost indispensable stage in the iron cycle in that shell. This results in its wide distribution, and practically all the iron that enters the zone of weathering must pass through this stage.

The next point of interest is the change into this state of the iron of oxygen-free compounds, *i.e.* chlorides and sulpho- and arseno-compounds. With regard to the first the problem is comparatively simple: once they pass into solution they cease to have any independent existence in the crust of weathering, for crystallization from vadose solutions is either unknown, or, if possible, connected with quite exceptional and rare conditions. This is easily explained by the common interaction between iron chlorides and the other salts present in vadose solutions, *e.g.* the alkali carbonates:—

$$2FeCl_3 + 3Na_2CO_3 = 6NaCl + Fe_2O_3 + 3CO_2.$$

The result of this reaction is the formation of colloidal ferric oxide $Fe_2O_3.nH_2O$, the greater part of which separates as a gel.

In those parts of the crust of weathering in which a reducing medium is established for an appreciable time there may result the formation of iron carbonate as the mineral *siderite* $FeCO_3$. Vadose forms of this compound occur either pure or contaminated with the carbonates of calcium or magnesium. Like calcium carbonate, ferrous carbonate is to some extent soluble in carbonated water, but is readily decomposed and concurrently oxidized. Hydrated ferric oxide separates from the solution. This explains the instability of $FeCO_3$ in the zone of weathering and its insignificant distribution. Vadose siderite, in contrast to hydrated ferric oxide, is not necessarily an indispensable phase in the iron cycle, but the bulk of the iron undoubtedly passes through the stage of bicarbonate $Fe(HCO_3)_2$ in solution.

The first stage in the transformation of the sulphides of iron is their oxidation and conversion into iron sulphate, as for example:—

$$FeS + 4O = FeSO_4,$$

$$\text{or } FeS_2 + 7O + H_2O = FeSO_4 + H_2SO_4.$$

The excess of sulphuric acid reacts with the salts of

alkalis or alkaline earths (carbonates, silicates) to form their sulphates.

Vadose sulphates of iron (copperas, perhaps certain varieties of iron alum) being ferrous-iron compounds and easily soluble in water, are still less stable than carbonates in the crust of weathering. After being converted into salts of ferric iron and encountering in natural solutions cations which have a greater affinity for the sulphate ion $SO_4''$, they give this up to the other metals (Na, K, Ca). This is confirmed by the infrequent occurrence of iron sulphates in the crust of weathering. Nevertheless this form plays no less a rôle than iron carbonates since, firstly, a considerable part of the iron enters the crust of weathering in the shape of sulphides, and, secondly, a certain part of the iron of another origin passes through the sulphide condition. As a matter of fact, we already know (p. 41) that one of the products of putrefaction of albuminous organic matter is $H_2S$; and when this reacts with the ferrous iron common in reducing media, it forms a new vadose colloidal mineral, *hydrotroilite*, $FeS.nH_2O$:—

$$H_2S + FeO = FeS + H_2O.$$

It is obvious that subsequent oxidation at once leads to the formation temporarily, at least, of iron sulphate. Analogous processes of weathering naturally embrace arsenious, antimonous, and other oxygen-free compounds of iron with the fundamental difference, however, that the stages corresponding to sulphates are so brief, owing to the instability of these compounds (arsenites, arsenates, antimonites), that the moment oxidation begins hydrated ferric oxide separates out.[1] Corresponding to hydrotroilite, the action of arsine ($AsH_3$) under reducing conditions may lead to the formation of vadose iron arsenide.[2]

As regards those minerals in which iron and magnesium silicates are in isomorphous mixture, we have already discussed the changes they undergo in connexion with the

[1] Mineralogists have described a few uncommon natural iron arsenates (sporodite $FeAsO_4.2H_2O$, pharmacosiderite $2FeAsO_4.Fe(OH)_3$, etc.), but these can hardly be regarded as of vadose origin.

[2] An observation of Bischof, cf. J. Roth, *Allgemeine und Chemische Mineralogie*.

forms of silica (p. 70). In this case it is evident that the iron separates on oxidation in the form of hydrated ferric oxide which covers the mineral with a brown film containing a certain amount of magnesium silicates. The cases in which iron replaces isomorphously the aluminium of aluminosilicates and those of pure ferrisilicates are somewhat different. With these forms we may be guided by analogy with the corresponding aluminosilicates, the more since the natural varieties of these minerals substantiate this analogy. For example, among the vadose minerals we find ferrisilicic acids: *iron kaolinite* $H_2Fe_2Si_2O_8.H_2O$,[1] and *chloropal* $H_2Fe_2Si_4O_{14}$, both of which are obviously analogous to the crystalline aluminosilicic acids with a kaolin structure, *kaolinite* and *pyrophyllite* (p. 87). We have reason for regarding these iron minerals as "residual" ferrisilicates of the first group, *i.e.* having as the basis of their structure a kaolin nucleus in which alumina is to a greater or less extent replaced by trivalent iron. Evidently in these ferrisilicates iron is much more strongly bound to silica than in others. But, however stable that union may be, it is nevertheless as in kaolinite (if not sooner), ultimately broken—perhaps, in certain cases, not without the assistance of organisms (iron bacteria). As regards the other ferrisilicates, we have no evidence that the union between silica and iron is particularly strong. Their decomposition proceeds even more rapidly than that of the corresponding aluminosilicates (melilite, chloritoid and chlorite groups). In this way we finally obtain hydrated ferric oxide, although, as we shall see below, it may not infrequently spend an extremely short time in the free state.

## 10. Hydrated Ferric Oxide and Vadose Ferrisilicates

In the active state colloidal hydrated ferric oxide is characterized by three fundamental properties: (1) like all mineral colloids while they are present in the upper part of

[1] Such a composition was found by Weinschenk for a pure variety of this mineral from Passau and referred by him to the nontronites. Under this name, however, there appears a mineral with different composition, $H_2Al_2Si_3O_{10}.2H_2O$, which can hardly be residual (*infra* p. 113).

the crust of weathering, it can alter its degree of dispersion, and in particular can change from the gel to the sol state and vice versa; (2) it can be reduced and then reoxidized; during reduction it may pass through the ferrous state or even become vadose native iron; (3) it can pass into true (molecular) solution via the ferrous state with $Fe''$ ions. The first property, as we mentioned, is general for all mineral colloids and gives rise to a series of changes similar to those we have described for alumina. Like alumina, with rare exceptions, iron is present in nearly all natural waters, and its content is of the same order. But in addition to this, soil workers have at their disposal a large number of observations showing the transfer, by solutions, of considerable amounts of iron. This transfer takes place over a comparatively small distance, and the main mass of iron is frequently deposited quite near the point of solution or peptization; but these deposits may again undergo solution or dispersion, and so on. As a result, we frequently observe soil horizons up to 0·5 m. thick which are quite devoid of iron, although formerly ferric oxide may have constituted 5-10% of their mass. It is necessary to bear in mind that this process does not occupy a long time according to the geological scale, but takes place in a matter of 50-100 years. We thus see before our own eyes the ability of hydrated ferric oxide to be peptized and coagulated. Experiments and observations confirm our views, and the presence of complex compounds of colloidal synthesis of hydrated ferric oxide with other colloids and, most of all, with colloidal active humus and silica. Among these latter we have Fe-humus sols and gels, which have already been mentioned (p. 57), and the coagels of hydrated ferric oxide with silica and their colloidal solutions, thoroughly studied by Reifenberg. In analogy to the synthetic *siallite-allophanoids* we will call these last *siferrite-allophanoids*. The bulk of the Fe-humus, and siferrite, colloids carry an electronegative charge.

Natural specimens of colloidal synthetic siferrite may be found among the many iron *hisingerites, pinguites* and other amorphous iron compounds. In these the $SiO_2 : Fe_2O_3$ ratio varies widely. For reasons connected with the conditions

under which these siferrites originate, they nearly always contain a greater or less amount of alumina, since in mutual coagulation phenomena with silica, ferric oxide and alumina there is a certain degree of isomorphism between the latter two substances. It is natural, therefore, that between the comparatively rare synthetic siallites and the similarly rare pure siferrites there exists a series of intermediate ferrisiallites which are much commoner. The ratios $SiO_2 : R_2O_3$ and $Al_2O_3 : Fe_2O_3$ in these likewise vary. Many varieties of the siallite synthetic acids that we have already described (p. 89*ff*) contain a certain amount of hydrated ferric oxide. While the majority of the siferrites are electronegative in character, proof of which will be given below, the possibility of the electropositive character of pure colloidal hydrated ferric oxide or of certain siferrites in which $Fe_2O_3$ predominates in the ratio $SiO_2 : Fe_2O_3$ cannot be denied.

The formation of vadose iron carbonates is one of the characteristics of that metal which sharply distinguishes it from aluminium in the crust of weathering. However small the distribution of these carbonates they definitely indicate the existence of solutions containing iron ions. It is true that these are the divalent ions $Fe''$, active only in a reducing medium, but we must not forget that the occurrence of the mineral $FeCO_3$ is far from accounting for the distribution of solutions containing dissociated salts of ferrous iron. Indeed, from these solutions neither carbonates nor any other ferrous salts can precipitate, and as a result of the direct oxidation of the solution hydrated ferric oxide will at once separate:—

$$2[Fe'' + 2HCO_3'] + O = Fe_2O_3.H_2O + 4CO_2 + H_2O.$$

But if natural solutions can contain ferrous ions in certain cases, it is obvious that these ions, just like other metallic ions, may be adsorbed by negatively charged colloids, among which may be both siallites and siferrites. Proofs that such a process takes place in nature are fairly numerous; thus, analyses of certain *hisingerites* show that in addition to magnesium there is some *ferrous iron* present (2-11%). The same has been shown for *polyhydrite, pinguite, neolites, saponites,* and many other minerals usually referred to the

group of clays or amorphous magnesian silicates. Ferrous oxide often plays the same part in adsorption systems of pure silica, this being very clearly shown by the amorphous mineral *webskyite* $[SiO_2 \ldots 2nOH']nMg(Fe)^{\cdot\cdot}$. In this case the " isomorphism " of magnesium and ferrous iron is clearly seen, but it will be more convenient to describe it in the discussion of magnesium.

The iron compounds taking part in the formation of vadose ferrous phosphates in all probability are in true solution. This is particularly so for the well-known mineral vivianite, $Fe_3(PO_4)_2.8H_2O$, the conditions of whose formation clearly show the part played by decomposing organic matter and consequently by reducing processes (bogs, bones of mammals, shells, etc.). As regards the vadose forms of ferric phosphates, they may be either the result of the oxidation of ferrous phosphates, such as we described for *oxykerchenite* and *beraunite* (p. 39), or the crystallization of adsorption compounds of ferric oxide and phosphoric acid analogous to those suggested for alumina (p. 90). Varieties of *kraurite,* $FePO_4.Fe(OH)_3$, may be formed in the latter way, although certain writers have suggested that they are formed in a like manner to oxykerchenite and beraunite. The genesis we have suggested is much more probable for *cacoxenite,* a ferric phosphate with a varying excess of the hydrated oxide, and which, although colloidal in appearance, has a microcrystalline structure.

The importance of the ability of ferric compounds to become reduced and to be re-oxidized has already been mentioned in the chapter on the cycle of oxygen. In this connexion there are some extremely interesting cases of the complete reduction of ferric oxide and the formation of a vadose form of native iron consisting of an independent variety of the polymorphous group of iron, devoid of any admixture of nickel and distinguished from other forms of iron by its crystallographic properties. Unfortunately the meagre data available give us little idea of how vadose native iron is formed. Apparently we have to do with highly dispersed ferrous oxide which falls into a strongly reducing medium. Native vadose iron, since it is not alloyed with

nickel, is still less stable than the forms of juvenile and cosmic iron.

### 11. The Absorption of Iron by Organisms

Iron in either of its states is taken up by organisms from solutions. Plant physiologists and agronomists regard it as one of the essential elements of plant food, and add it to the list of mineral "organogens." It has been found that in artificial cultures the lack of iron salts in the nutrient medium prevents proper plant development. Iron is thus an essential element of living matter, and analyses constantly show that it is present in various organisms both of vegetable and animal origin, but in very varying amounts. In certain organisms it is a necessary part of their bodies (*e.g.* iron bacteria), in others it may exceed 10% of the living matter, but in the majority of cases it is considerably less. Cultivated plants contain only hundredth or thousandth parts of a per cent. of iron (dry matter), but among these are found great fluctuations within these limits. Thus, potato contains about 2 mg. $Fe_2O_3$ per 100 g., while cucumber growing nearby on the same soil may contain up to 30 mg. and garlic up to 60 mg.

What we know of the functions of iron in the organism seems to show that these may be various. In certain lower organisms, for example, the oxidation of iron is a normal part of the respiratory process; in green plants iron stimulates the formation of chlorophyll. The absence of iron from their nutrients brings about a disease known as chlorosis, shown by the cessation of chorophyll formation and the subsequent death of the plant. An analogous part is played by iron in animals, where it acts as a stimulant on the blood-forming centres. This analogy is confirmed still further by the similarity in the chemical nature of these two pigments: the green chlorophyll and hæmoglobin, the red pigment of animal blood. One fundamental difference, however exists: iron does not enter into the composition of chlorophyll, whereas it is an essential element of hæmoglobin.

Corresponding to the different functions there ought to be different forms of iron compounds in organisms. Both in

animals and plants iron, in a definite form, plays the part of a catalyst, in addition to which it is accumulated in animals in the form of hæmoglobin. The observations of certain physiologists that iron is also necessary for non-chlorophyll bearing plants indicate the possibility of other iron compounds. There can remain no doubt, therefore, that a great mass of iron passes through a stage in combination with living matter, and it is quite possible that this is an inevitable phase in the cycle of iron compounds.

## 12. The Crystallization of Gels and Coagels of Ferric and Aluminium Hydroxide Systems

The chemical composition of any compound of colloidal synthesis, be it a complex coagel, or a simple gel with adsorbed ions or with water only, does not, in general, follow any strict stoichiometric rules. If we remember that in colloidal reactions one of the components is always a polymolecular micelle whose molecules have different states and compositions depending on their position, either on the surface or inside the micelle, then the reason for this becomes apparent. It is also obvious that consequent on the internal changes in the gel (solidification, dehydration, crystallization) we must not expect, *in all cases,* the formation of a homogeneous, simple, crystalline compound whose composition follows stoichiometrical rules. In the crystallization of gels, *in general,* we obtain a complex body—a system containing a number of components corresponding to the states and composition of the molecules which were present in the gel immediately before its crystallization. An excellent example of this is found in the natural forms of hydrated ferric oxide, which until quite recently were regarded as molecular hydrates. The commonest of these are :—

(1) *Limonite,* of which there are many varieties (brown iron ore, bog iron ore, stilpnosiderite, pea ore, kidney ore). Ortstein is not properly referred to this group.[1] All these forms were regarded as varieties of a definite hydrate, $2Fe_2O_3.3H_2O$.

[1] Ortstein is always a very complex mineral body in which hydrated iron oxide is only one of the many constituents.

(2) *Göthite,* with its varieties (needle ore from Pschibram, *lepidocrocite,* etc.), which were supposed to be $Fe_2O_3.H_2O$. Besides these there are the lesser known :—

(3) *Xanthosiderite,* richest in water, $Fe_2O_3.2H_2O$, which was regarded as an analogue of bauxite.[1]

(4) *Hydrogöthite,* $3Fe_2O_3.4H_2O$, and

(5) *Hydrohaematite* (turgite), with least water, $2Fe_2O_3.H_2O$.

Recent careful investigations using thermal analysis,[2] however, show that there is only one real hydrate, the monohydrate, $Fe_2O_3.H_2O$, which ought to correspond to a pure variety of göthite. The other natural compounds of hydrated ferric oxide consist of *solid solutions* of water either in *haematite,* $Fe_2O_3$ (including hydrohaematite and turgite), or in the *monohydrate* (limonite, brown iron ore, and several varieties referable to göthite, etc.). It is obvious that besides these there occur colloids (gels) which have not yet undergone crystallization (pea ore). The formation of the first category (hydrohaematite, turgite) may be conceived as follows. We have a colloid whose micelles consist of $Fe_2O_3$ molecules with those on the surface hydrated; during crystallization dehydration takes place, and the water set free enters into solution in the $Fe_2O_3$, assuming the character of intermolecular (zeolitic) water. In the second group (limonite, brown iron ore) the micelles of the original colloid consist of the monohydrate, and the surface is hydrated to a greater degree. During crystallization only the latter is dehydrated and the free water goes into solution in the monohydrate of ferric oxide.[3] In any case, the change from gel into solid solution is extremely important, for it allows us to hazard an opinion as to the nature of other, more complex, systems arising from complex gels containing ferric oxide.

But if a complex gel results in the formation, after its internal changes and aging, of a similarly complex formation of the solid solution type, then at the same time some

[1] Actually, bauxite is not a definite mineral, but a mixture of $Al_2O_3.nH_2O$ and $Fe_2O_3.nH_2O$. The dihydrate $Al_2O_3.2H_2O$ is not known.

[2] H. S. Kurnakov and E. J. Rode, *loc. cit.* Also H. B. Weiser, *loc. cit.*

[3] The necessity of distinguishing hydrated gels of ferric oxide from the hydrated oxide itself was first pointed out by Van Bemmelen.

of its properties frequently predetermine the definite character of those compounds that enter into the solid solution system. Thus, the surface molecules with their adsorbed ions ought to form the beginning of a stoichoimetric compound, and since the colloidal adsorption complex can adsorb at the same time either different cations or different anions from complex natural solutions, it is obvious that in such an adsorption system we have in embryo a future isomorphous mixture of definite compounds; and even the regularities of isomorphism, as we shall see later, follow directly from the properties of the adsorbed ions and the nature of the adsorption complex. Much, however, in the obscure process of the aging of gels remains unknown. It would be of very great importance if we could elucidate those properties of a complex gel which predetermine the formation of complex radicals and addition products. They may be found from a study either of the adsorption of " complex ions," or of the diverse phenomena of mutual coagulation, but at present that is only a suggestion.

In the meantime the most important and most valuable materials from our point of view are the facts of natural formations, so let us return to them. It may be regarded as fully established that the various forms of natural ferric oxide, limonite, brown iron ore, etc., consist of different phases in the transition of the gels, $Fe_2O_3.nH_2O$ and $FeO(OH).nH_2O$, to solid solution systems with the monohydrate predominating. We may also take as being fully established the formation, within the crust of weathering, of crystalline varieties of FeS, secondary *pyrites* and *marcasite*. These minerals, characteristic of many sedimentary rocks, containing organic residues (carbonaceous shales, coal), and frequently, like vivianite, directly connected with different organic remains (bones of vertebrates, shells, etc.), crystallize in a reducing medium. On quitting that sphere they are again weathered like the primary sulphides (p. 99), marcasite being especially rapidly oxidized and decomposed The initial material for their formation is a colloidal system containing *hydrotroilite* ($FeS.nH_2O$), and, in all probability, $H_2S$ dissolved in the adsorbed water. The analyses

of certain marcasites have shown the admixture of sulphuretted hydrogen.[1]

We have already remarked (p. 104) on the possibility of the formation of microcrystalline, yet colloid-like phosphates of ferric iron as a result of the crystallization of colloidal ferric oxide containing adsorbed phosphoric acid (cacoxenite).

The further fate in the crust of weathering of colloidal systems containing iron and silicon is apparently still an open question. The systems are :—

(1) Iron silicates :—

$$[SiO_2 \ldots 2nOH']nFe^{\cdot\cdot},$$

(2) Those diverse colloidal condensation products which are united in the group of ferrisilicic allophanoids and their derivatives, *i.e.* systems containing adsorbed cations :—

$$[SiFe \ldots 2nOH']2nR^{\cdot}(nR^{\cdot\cdot}) \text{ (p. 102)}.$$

The analogy between ferrisilicic and aluminosilicic allophanoids, and the wide distribution of mixed alumino-ferrisilicic forms, compels us to regard all these formations together as one great group, united by many general features both of composition and structure, and their probable reactions. In the great majority of cases very little can be said about the further changes of these complex gels. Among the reasons for this are the insufficient attention paid by mineralogists to these complex compounds, the absence of suitable methods for the study of complex colloidal bodies, and, finally, the simple fact that further changes can take place only in the deeper parts of the lithosphere. Their products are found in metamorphic rocks in such an altered state that to discover the connexion with the original substance is not always possible. Nevertheless, we have certain factual material at our disposal, and from it we may make some hypothetical generalizations. Among this material we find accounts of the singular minerals *gymnite, deweylite,* and *pseudodeweylite*. All these seem to be typical mineral gels, adsorption compounds, and there is little doubt that such is their nature. As might be expected analyses do

[1] Naumann-Zirkel, Elemente der Mineralogie, 1907, p. 424.

not allow us to give definite formulæ to them, and the attempts in this direction have not been very successful.[1] The analyses indicate a magnesian silicate as the basis of the colloidal system, but in addition it contains a certain quantity of sesquioxides, calcium and ferrous oxide. Of greatest interest from our point of view are the observations of individual investigators (Websky, Foggy) on *certain varieties of these minerals which show clear indications of crystallization.*[2] The determination of the final forms of the crystalline compounds has not proved possible. Another analogous case is found in the group of vadose minerals known as *saponites*. These are compact, amorphous masses of indefinite composition, in which the principal part is played by a magnesium silicate, with a definite, and sometimes significant, admixture of an aluminosilicate compound of ferrous oxide and calcium. They are frequently described as alteration products of other magnesian silicates and especially of serpentines. This is because they usually occur in contact with the "primary" material, and when this "primary" material is absent the new formation is said to be in a "secondary" position. Actually it may be formed anywhere by colloidal synthesis. The proximity of other magnesian silicates, obviously, may play a great part, but the material which they supply undergoes such radical changes that to speak of the new compounds in such cases as alteration products of the original minerals is hardly correct. But an interesting fact is the occurrence among the saponites of varieties with clear indications of crystallization (*bowlingites*).[3] Their composition apparently approximates to that of the chlorite group.

A much more important fact, however, is the formation, within the crust of weathering, of the mineral *glauconite* and minerals of the *paligorskite* group.

*Glauconite* is a crystalline potassium ferrisilicate, and from its composition and structure may be referred to the

[1] *Cf.* J. W. Mellor, Theoretical and Inorganic Chemistry, Vol. VI, p. 423.
[2] H. Leitmeier, Deweylite und pseudodeweylite, *Handbuch der Mineralchemie* von C. Doelter, Dresden, 1914. Bd. II, pp. 436-439. Also Mellor, *loc. cit.*
[3] Leitmeier, *loc. cit.*, pp. 443-444.

chlorite group. In the acid radical iron may be replaced by aluminium, and as base Mg,Fe", or Ca may replace potassium. It is found in certain submarine parts of the zone of weathering where it settles to the bottom as a fine gel forming films and filling up the shells of sea animals. Crystallization takes place with a change in colour from brownish yellow to green, and may be followed under the microscope.[1] The fact that its formation is confined very strictly to certain localities makes us think of conditions that are favourable to the precipitation of ferrisilicic gels of definite composition and containing adsorbed cations, especially potassium. It is possible that the concentration of potassium is sufficient only in those organisms whose shells are filled with the gel. But potassium is not always the predominating cation, magnesium and ferrous iron frequently exceed it.[2] The glauconite in its final form consists either of minute crystals, which frequently form a kernel in shells of globigerina and other animals, or of a fine green pigment in silty deposits. Glauconite is a good example of the crystallization of complex aluminoferrisilicic products of colloidal synthesis with the formation of a ferrisilicic nucleus similar to that of the aluminosilicates of group IV (p. 83).

*Paligorskites* are hydrated aluminosilicates of magnesium in which the latter is replaced to some little extent by Ca, Fe", Mn", etc. Exceptions to this are calciopaligorskites in which Ca predominates among the bases. In analogy to the paligorskites the magnesian ferrisilicates form a special subgroup called *xylotiles*. From their chemical structure the former are addition products of the orthosilicate nucleus $H_8Mg_2Si_3O_{12}$ and the aluminosilicic group $H_{10}Al_2Si_4O_{16}$, and the latter of the same nucleus with the group $H_6Fe_2Si_3O_{12}$.[3] They thus stand more closely to the second group of aluminosilicates. These vadose minerals have a fibrous crystalline structure, although in outward appearance they are corky, filmy and otherwise colloid-like. According to a detailed investigation of paligorskites and re-

[1] L. W. Collet, Les depots marins. Paris, 1908. pp. 144-145. Mellor, *loc. cit.*, p. 919.
[2] *Ibid.*
[3] Mellor, *loc. cit.*, p. 825.

lated magnesium silicates "they are formed under the normal conditions of the crust of weathering from either hot or cold aqueous solutions."[1] This is an extremely important conclusion and indicates that we are dealing not with *residual* but with *synthetic* products of weathering, with the results of the interaction of solutions. It should be added that in addition to the paligorskites and xylotiles found in large masses, they also occur as *soil* formations,[2] a fact which can thus be satisfactorily explained. This will be done in the discussion of magnesium (p. 137*ff*). In the present instance what is important is that we have here the crystallization of aluminosilicic products of the colloidal complex, with the formation of compounds of the type characteristic of the second group of aluminosilicates.

Let us formulate the conclusions we have reached regarding the changes undergone by iron, aluminium and silicon compounds in the crust of weathering.

1. The crystallization of mineral gels in many cases takes place in the crust of weathering.

2. This process embraces not only the gels of simple compounds such as the hydrated oxides of silicon, aluminium and iron, but also complex colloidal systems, the natural products of adsorption synthesis: aluminosilicic and ferrisilicic coagels with adsorbed cations.

3. The crystallization of aluminosilicic gels in the crust of weathering forms the basic outlines of the chemical structure of certain definite groups of aluminosilicates.

Such are the processes preparing the material leaving the crust of weathering for its further changes in the deeper sheaths of the earth's crust. What these changes are, and what relation vadose minerals bear to chlorite and other schists, are questions outside our purview. To turn back for a moment and with that to conclude our review of the cycle of iron compounds, we should note that they provide an excellent example of those relations between colloids and crystalloids in the crust of weathering which were pointed out in his time by Cornu. Table I may serve as an illus-

[1] A. Fersman, *Trans. Acad. Sci.* (Russ.), 1913, **32**, 311.
[2] B. Polynov, Ortstein horizon of soils, *Ann. Dokuchaiev Soil Com.*, 1914.

tration of these relationships. In the first column are the known and most probable forms of those " mutable," active

TABLE I.

| I. Active Mutable Forms of Vadose Iron Compounds | II. Products of the Crystallization of Mutable Forms ; Formation of Solid Solutions and other Results of the "Aging" of Gels |
|---|---|
| 1. Organomineral compounds of living matter (haemoglobin, etc.). | |
| 2. Coagels with active humus. | |
| 3. Gels of ferric oxide: films, efflorescences, pea ores, etc., $Fe_2O_3.nH_2O$. | Hydrohaematite, turgite: $Fe_2O_3.qH_2O$, limonite, brown iron ore: $FeO(OH).qH_2O$. |
| 4. Coagels with silica: ferrisilicic colloidal acids of the type: $[SiFe \ldots nOH']nH'$. | Crystalline ferrisilicic acids: *nontronite*, $H_2Fe_2Si_3O_{10}.2H_2O$. |
| 5. The same but with adsorbed cations: $[SiFe \ldots 2OH']nR''(2nR')$. | *Glauconite, hisingerite, pinguite,* etc. |
| 6. Complex coagels of the type: $[SiFe \ldots 2nOH']nMg''(2nH')$. | *Xylotiles:* $pH_8MgSi_3O_{12}.qH_6Fe_3Si_3O_{12}$. |
| 7. Gels with adsorbed phosphoric acid: $[FeO(OH) \ldots 3nFe(OH)_2']nPO_4'''(3nOH')$. | *Cacoxenite:* $FePO_4.qFe_2O_3.pH_2O$. |
| 8. Ferrous ions in solution ($Fe''$). | *Vivianite:* $Fe_3(PO_4)_2.8H_2O$. *Siderite:* $FeCO_3$. *Copperas:* $FeSO_4$. |
| 9. *Hydrotroilite:* $FeS.nH_2O$. | *Secondary pyrites, marcasite:* $FeS_2$. |
| 10. Native vadose iron. | |

and predominantly colloidal, compounds of iron which play such a vital part in its cycle. The horizontal line in the lower part of that column between the seventh and eighth groups forms distinguishes the region of reduction processes. In the second column are the corresponding crystalline products. These are predominantly exothermic, and are the forms in which iron quits the crust of weathering for the

deeper zones. The products of a reducing medium, given in the lower part of the table, are the more active compounds, capable, as they are, of being oxidized (*e.g.* vivianite). It is obvious that many possible forms are not in the table, but the aim of the latter is only to show known relationships between the two types of compounds in the crust of weathering.

### 13. Compounds of Titanium, Zirconium, Tin, Boron and Vanadium

Silicon, aluminium and iron, in their cycles in the crust of weathering encounter, as we have already seen, innumerable other elements, some acting as bases and others as parts of simple or complex acidic radicals or additive groups. Of many of these elements we have nothing to say, since they either do not play any significant part in the crust of weathering, or, if they do, very little is known about them. The commonest elements are reviewed later in their proper place, but it is necessary to mention certain, less common, which nevertheless apparently play a part analogous in many respects to those we have already discussed. The first of these is titanium which belongs to the same chemical group as silicon and gives natural compounds similar to those of the latter element. It is distinguished from silicon by its more metallic character, which is clearly expressed in the basic properties shown by the naturally occurring oxide *rutile* ($TiO_2$), in contrast to the acidic properties of quartz. Titanium is capable of several degrees of oxidation: $Ti_2O_3$, $TiO_2$, $TiO_3$, but the dioxide is the only one occurring to any extent naturally (*rutile, anatase, brookite*). Analyses of rutile and other titaniferous minerals frequently show the presence of a small admixture of the sesquioxide $Ti_2O_3$, but this does not form individual minerals. In isomorphous mixture with $Fe_2O_3$ and $Al_2O_3$ titanium sesquioxide may also be encountered in various aluminosilicates.

The compounds of titanium which are *primary* for the crust of weathering are the varieties of $TiO_2$: *rutile, anatase, brookite;* a series of *titanates,* salts of metatitanic acid, *e.g. perofskite* ($CaTiO_3$) minerals of the *ilmenite* group ($FeTiO_3$),

in which Fe, Mg, Mn, may isomorphously replace each other; finally a group of more complex compounds: *titanosilicates*,—salts of a complex acid of the type $R^{II}TiSiO_5$. The commonest of these is *sphene* or *titanite*—$CaTiSiO_5$, but barium, manganese and other titanosilicates are known. Much rarer are the *titanoniobates* and *silicotitanoniobates*. Unfortunately information about the weathering of these minerals is extremely meagre, but it seems probable that one of the products of weathering is *secondary rutile*, which separates on the decomposition of more complex titanium compounds. This titanium dioxide at first appears as anatase, which then passes into the more stable rutile. It seems quite justifiable to assume that during these changes titanium dioxide passes through the same phases as does silica on the decomposition of silicates, and may frequently pass into solution. This assumption is necessary, otherwise it would not be clear how titanium occurs in living matter in which analyses have shown it to be present in much the same quantity as arsenic, boron, lead and fluorine.

The few analyses available show a relative accumulation of $TiO_2$, in certain cases, in the upper (soil) horizons of the crust of weathering, where its content reaches 2% and more, while its average for the earth's crust is 0·5%, and for the lithosphere 0·4%. Judging by a few analyses its content in marine terrigenic deposits reaches 0·7%, while in the deep sea deposits it is about 0·5%.[1] In what actual vadose compounds titanium is accumulated in the soils we do not know. It is possible that it enters into complex aluminosilicic colloidal systems together with silica and the sesquioxides. It is evident that before it leaves the crust of weathering titanium undergoes certain changes, but of these we have no clear knowledge.

We have still less to say of the other members of the same chemical group: zirconium, tin and lead. The first of these, besides the natural zirconium oxide (*baddeleyite*) $ZrO_2$, and *zircon* ($ZrSiO_4$), gives a series of rare primary silicozirconates[2] of sodium and calcium which are usually

[1] F. W. Clarke, Data of Geochemistry, 5th ed., 1920.
[2] *E.g.* eudialyte, zirconium pyroxenes, etc.

regarded as the products of pneumatolytic action. The clear indications of decomposition (*e.g.* of *mosandrite,* rare in the fresh state) are ascribed, not to weathering, but to later *vein* processes. At the same time there exist direct indications of the hydration of zircon and the formation of colloidal products from it. Varieties of zircon with a high water content (up to 10% and greater), and also admixtures of calcium, magnesium, and other bases (possibly adsorbed), are therefore correctly described as of secondary origin (*malacone, alvite, auerbachite,* etc.).[1] There are no data on its content in soils and living organisms.

Tin exists as a primary mineral in the form of *cassiterite,* $SnO_2$, the only tin ore. In addition, rare occurrences of native tin (volcanic emanations of Stromboli and elsewhere), and a calcium stannosilicate *stokesite* ($CaSnSi_3O_9.H_2O$), are known. Of the products of weathering nothing is known, but cassiterite is known to be very stable. Such products must exist, however, for analyses have shown the presence of tin in the composition of plants.

Lead acts as a base, and so it will be more appropriate to discuss it later with other metallic elements.

*Boron* is found in a large number of primary silicates, in which it replaces aluminium and forms borosilicates in analogy to the aluminosilicates (*datolite, tourmaline, homilite, howlite, danburite*), and not infrequently it is found in isomorphous mixture with aluminosilicates (*dumortierite*). In addition, various borates are well known as products of volcanic and post-volcanic activity. The great solubility both of the weathering products of borosilicates and of juvenile borosilicates leads to the accumulation of secondary borates, predominantly in saline lakes with other chemical deposits (*boracite* $Mg_7Cl_2B_{16}O_{30}$, *tincal* $Na_2B_4O_7.10H_2O$ (natural borax), *sodaborocalcite* $NaCaB_5O_9.6H_2O$, etc.). These lacustrine accumulations are the typical form of boron compounds in the crust of weathering. On its rôle in organisms nothing is known except that it is essential even in minute quantities for the life of the plant, and it is found in all cases when it has been looked for, although only in traces.

[1] J. W. Mellor, Treatise on Theor. and Inorg. Chem., Vol. VI, p. 844*ff*.

The fact that some or other element is present in organisms does not prove that it plays any significant part in the biosphere and crust of weathering. There is no doubt that in organisms, as in soils, all the elements occurring in the lithosphere may be found in some quantity or other. In those cases, however, when an *obvious concentration* of an element in the composition of living matter or some or other formation in the crust of weathering is noted, a specific rôle must at once be suspected and attention paid even to rare elements.

One of such comparatively rare, and yet indubitably important elements is *vanadium*, whose content in the earth's crust only amounts to a few hundredths of one per cent. According to the latest calculations of Clarke and Washington, making use of 5,179 analyses, vanadium in the form of its sesquioxide $V_2O_3$ makes up 0·026% of massive rocks, *i.e.* only half as much as chlorine, and less than zirconium, barium, nickel and fluorine, and of the same order as strontium.

Its primary juvenile forms are concentrated, for the most part, in basic igneous rocks rich in magnesium and iron. In these its content increases to 0·05%. Nevertheless, individual primary vanadium minerals are little known. The vanadium mica *roscoelite* found in porphyrite in California contains about 24% $V_2O_3$, and the rare mineral *ardennite* with 9% is an extremely complex vanadosilicate of manganese with the empirical formula—

$$H_{10}Mn_{10}Al_{10}Si_{10}V_2O_{55}.$$

Apparently the main masses of vanadium occur in the form of minerals in which small amounts of $V_2O_3$ isomorphously replace the alumina of aluminosilicates. Much more numerous and diverse are the secondary vanadium minerals, which owe their origin to *hydrothermal* (*e.g. vanadinite*, lead vanadate) and *weathering* processes.

In the latter case the concentration reaches quite noticeable values. It occurs in sedimentary rocks rich in organic remains. For example, in lignite from the Argentine $V_2O_3$ amounts to 38% of the ash content, and the same vanadium

content is found in certain Peruvian coals. The mineral matter of Nevada asphalt contains about 30% $V_2O_3$, and in the mesozoic sandstones of Colorado and Utah vanadium occurs as the minerals *tyuyanunite* $Ca(UO_2)_2V_2O_5.4H_2O$, and especially as *carnotite* $K_2(UO_2)_2V_2O_5$, *i.e.* in the form of calcium, and potassium, uranyl vanadates. Such deposits are worked for these ores. They occur in the same form in veins in limestone in Fergana, where in addition to the above minerals there are also found: *alaite* ($V_2O_5.H_2O$), *turanite* ($5CuO.V_2O_5.2H_2O$), *tangeite* ($2CaO.2CuO.V_2O_5.H_2O$).

Throughout its vadose compounds vanadium acts a pentavalent element with a clearly expressed acidic character, while in its primary forms it isomorphously replaces aluminium, appearing as a trivalent element.

To return to the vadose forms of vanadium we have seen that it is largely concentrated with organic residues, as is clearly shown in the asphalts (Utah), and we must conclude that organisms play some part in the concentration of vanadium in the crust of weathering. The occurrence of vanadium in plant ash, as we have already noted, is by itself not important in this connexion. Of much greater significance in this connexion are the observations on its rôle in the formation of the blood of ascidium. We are thus convinced that vanadium plays an active part in organisms analogous to that of iron, and consequently its presence in the crust of weathering is shown by a series of changes of which we have only a superficial conception. The most probable suggestion seems to be that the concentration of vanadium in the crust of weathering is brought about by definite groups of organisms in deposits of the sapropel type.[1]

[1] Vanadium in the blood of ascidium was observed in members of the *Phallusia* genus. These are the simplest of the ascidium, leading a separate existence and living mainly in the coastal part of the sea.

CHAPTER IV

# THE CYCLES OF THE ALKALI AND ALKALINE EARTH METALS, CHLORINE, SULPHUR AND PHOSPHORUS

## 1. The Alkali and Alkaline Earth Metals

Following iron in the distribution series we have the alkaline earth and the alkali metals: calcium (3·20%), sodium (2·35%), potassium (2·27%) and magnesium (2·07%). Calcium clearly predominates over the others, sodium and potassium are nearly equal in amount, while magnesium is somewhat lower. Such a relationship also holds when the figures for the composition of the lithosphere by itself are considered: calcium (3·47%), sodium (2·46%), potassium (2·46%), magnesium (2·24%).

In the great majority of juvenile (igneous) rocks we find compounds of all these four elements, but their relative quantities vary very greatly, and are sometimes used in the classification of individual groups of rocks. Thus, in typical rocks formed from an acid magma (granites, quartz porphyrites, trachytes, liparites) the sum of the alkalis ($K_2O + Na_2O$) is usually $1\frac{1}{2}$, 2 and even 3 times that of the alkaline earths ($CaO + MgO$), and may reach 7-10%. Of the two, potash usually predominates, but this predominance corresponds approximately to the higher atomic weight of that element, and the molecular ratio $K_2O : Na_2O$ may be taken as nearly unity. Exceptions are, of course, encountered (soda granites, dacites, granodiorites). In the ratio $CaO : MgO$ the first usually predominates, and may frequently do so even in atomic, and consequently in the molecular, ratios. The acid magma is by far the most widespread.

Potassium in these rocks occurs, for the most part, as potash feldspars: *orthoclase, sanidine* and *microcline,* which

are distinguished from each other by their optical properties. Microcline is most resistant to weathering, and is usually found in the residual material in a fairly fresh state. Certain products of the disintegration and weathering of morainic deposits, already devoid of most of the primary minerals, frequently contain many microcline grains, which stand out clearly on microscopic examination.

Sodium and calcium are represented mainly by acid *plagioclases*, in which the soda member (*albite*) predominates over the lime (*anorthite*). The first also occurs in the form of individual soda feldspars: *albites* and *anorthoclases*.

Magnesium is common in acid rocks as the magnesian mica (*biotite*) and occasionally there also occur members of the *augite* and *hornblende* groups (granodiorites).

In rocks of a basic magma we find, in contrast, an obvious and sometimes very marked predominance of the alkaline earth metals, even to the almost complete disappearance of the alkalis, or the presence only of traces, as, for example, in certain *dunites* and *pyroxenites*. Among the more widely diffused basic rocks, *e.g. gabbros, basalts, diabases*, the ratio of the sum of alkaline earths ($CaO + MgO$) to that of the alkalis ($K_2O + Na_2O$) is usually more than 3 and sometimes reaches 6, while the sum of the alkalis varies from 3 to 5%. The sodium of the basic magma is usually 2-2½ times that of potassium. Of the alkaline earths in the commonest varieties—basalts, andesites, diorites, diabases, gabbros—calcium frequently predominates, but no more so than its higher atomic weight warrants. In ultra-basic rocks (*peridotites, pyroxenites, dunites*) magnesium is considerably in excess and reaches 40% or more. Potassium is usually at a minimum in basic rocks and rarely exceeds 2%. Magnesium in these rocks occurs in *augite* and *hornblende*, which contain a metasilicate nucleus, and also in the orthosilicate *olivine* ($Mg_2(Fe_2)SiO_4$). Calcium and sodium are in the form of basic plagioclases, characterized by the predominance of anorthite (*labradorite, bytownite*) and pure *anorthite*, $CaAl_2Si_2O_8$, and also by isomorphous mixtures of calcium and magnesium silicates. Finally, there is a particular alkaline magma in which the alkali metals pre-

dominate considerably over the alkaline earths. Their content frequently reaches 15-20%, and is frequently 10 times the content of the alkaline earths. Sodium and calcium usually predominate in their respective groups. In these basic rocks potassium and sodium occur in the form of alumino-silicates belonging to the felspathoid group, which according to their structure may be referred to the second group of alumino-silicates (p. 81). Among them are: the potassium aluminosilicate *leucite*; the potash-soda *nepheline*; *sodalite*, *cancrinite*; the lime-soda: *haüynite* and *nosean* and finally, the soda-lime-magnesia, *melilite*, which we already know. The alkali and alkaline earth metals are present in metamorphic rocks (crystalline schists) also, but, in addition to the compounds enumerated, there are many new forms, the diversity of which is especially noticeable with magnesian (talc, serpentine, group of chlorites) and calcium minerals (garnets, epidote, vesuvianite, wollastonite, scapolite, etc.). This list of the compounds of the alkali and alkaline earth elements gives the primary (predominantly juvenile, but partly phreatic) forms in which these elements appear in igneous and metamorphic rocks in the zone of weathering.[1] The first stages of weathering, as we have already noted, ought to be marked by the formation of the carbonates of these elements, in which form they take part in a number of reactions. But before taking up the consideration of these interactions, it is interesting to make a number of comparisons which very clearly emphasize the differences in the fate of these elements in the zone, and crust, of weathering. Let us contrast, first of all, the percentage content of these elements in primary massive rocks, the lithosphere and the hydrosphere:—

| | Massive Rocks. | Lithosphere. | Hydrosphere. |
|---|---|---|---|
| Ca ... | 3·63 | 3·47 | 0·05 |
| Na ... | 2·85 | 2·46 | 1·14 |
| K ... | 2·57 | 2·46 | 0·04 |
| Mg ... | 2·09 | 2·24 | 0·14 |

1 It should be noted that in addition to these minerals there are a number of juvenile forms of the alkali and alkaline earth compounds that are identical in composition to the vadose forms (*e.g.* alkali chlorides of volcanic origin, juvenile calcite, etc.). It is obvious that their changes in the zone of weathering will not differ from those of the vadose forms.

We see that in the lithosphere the amounts of the different elements have changed relative to those in the massive rocks. But the change in the hydrosphere is especially radical: sodium greatly predominates, magnesium is second, but much less, whilst calcium and potassium come last and are about equal. Remembering that we are not dealing with an established equilibrium, but with an ever active process, we arrive at the following conclusion: *while all the sodium of any definite mass of primary rock attains the highest degree of dispersion for the crust of weathering, i.e. molecular solution in water, and passes in this way into the hydrosphere, only part of the calcium, potassium and magnesium contained in the same mass of rock attains that state; the other part remains in the crust of weathering in insoluble forms which have either not yet managed to dissolve, or have been precipitated from aqueous solutions.* In order to discover just which parts remain in these forms and in which stages of the cycles of weathering, it is necessary to consider the contents of these elements in river water. This serves as an intermediary between massive country rocks and the hydrosphere, since it supplies the latter with these elements. In this we shall take sodium as being 100 and recalculate the others on this basis, so that the comparisons may be clearer. We thus obtain:—

| | Massive rocks. | River water. | Hydrosphere. |
|---|---|---|---|
| Ca ... | 127 | 330 | 4 |
| Na ... | 100 | 100 | 100 |
| K ... | 90 | 33 | 3 |
| Mg ... | 73 | 50 | 12 |

Thus, we see that the calcium of a certain mass of country rock goes into solution in river water 2·6 times faster than the sodium contained in the same rock, yet all the sodium reaches the hydrosphere, while only 3·1% of the calcium remains in that medium. Since we have repeatedly remarked on the enormous quantity of calcium carbonate removed by marine organisms for the construction of their skeletons, this last conclusion does not appear paradoxical. At first sight, it may not be quite clear why calcium should

pass into river water more rapidly than sodium, but the explanation will be given later.

Potassium is removed to much less extent than sodium, more than 60% remaining in the products of weathering, and of the remainder only 3·3% is found in the composition of the hydrosphere, while more than 30% is removed in some or other form from the solution during its entrance into the sea. Magnesium leaves behind more than 30% of its original mass in the products of alteration; of the remainder 16·4% reaches the waters of the oceans, and more than 50% is removed from solution as it enters the sea. The figures we have just quoted do not pretend to great accuracy, for in calculating them many approximations have been made, but they apparently satisfy the order of the corresponding magnitudes and the ratios between them.[1]

Thus, on the basis of these preliminary general considerations we may put forward, conjecturally, the following conclusions:—

1. Of the elements we have considered, sodium gives the least stable compounds in the crust of weathering; its cycle of changes takes place more quickly than the others, and its commonest form in the crust of weathering is the molecular solution of sodium salts.

2. The most stable and most widely diffused vadose calcium compounds are formed when its solutions in river water fall into marine basins.

3. The vadose compounds of potassium that are most widespread, and of longest existence, are connected with the weathering products of dry land, but a certain number of forms belong to submarine weathering.

4. Magnesium gives an important number of vadose forms connected with the weathering products of dry land, but a much more important number formed by the processes of submarine weathering.

And now let us see to what extent these conclusions are supported by observations and facts.

1 *Cf.* V. M. Goldschmidt, Grundlagen der quantitativen Geochemie. Fortschr. der Min., 1933, **17**, 112-156.

## 2. The Dissolution of the Alkali and Alkaline Metals

Observations on the weathering of igneous rocks and their constituent minerals have frequently led petrographers to the general conclusion that basic rocks weather more rapidly than the acid, the basic feldspars (anorthite predominating) more quickly than the acid, and the dark ferromagnesian silicates more rapidly than the lime-soda minerals.[1] It is necessary to note that this conclusion is the result of simple observation in which no account was taken of intermediate forms, the effect of the disintegration of primary minerals only being noted. Such disintegration might have resulted from a purely mechanical action—the pulverization of crystals into pieces beyond the limits of observation, and of unknown constitution. In such an account it is natural that minerals having a highly developed cleavage (micas) and little hardness, and also minerals that readily change their appearance in the initial stages of weathering, should be relegated to the category of easily weathered minerals even in those cases where they might have retained their chemical structure intact.

A deeper study of the products of weathering leads to a somewhat different result. As regards the feldspars, we must acknowledge that the basic members do weather, in general, more rapidly than the acid, and this is true for both the initial stages and the final disintegration of the mineral. This is also confirmed by the resistance of the minerals to acid treatment. The extreme member of the basic series of plagioclases, *anorthite,* is comparatively easily decomposed by dilute hydrochloric acid with separation of silica, whilst the extreme of the acid series, *albite,* is not affected even by much stronger acid. And here we have an example of the greater resistance to weathering of certain primary sodium compounds as compared with primary compounds of calcium. If we remember the wide distribution of feldspars, it becomes apparent that these properties ought to be reflected in the relative amounts of calcium and sodium in river water.

Somewhat different results are obtained from the study of the weathering of magnesian silicates. While the first

[1] *Cf.* E. Weinschenk, Grundzüge der Gesteinskunde, 2nd ed., 1906.

stages (discoloration, *i.e.* separation of iron silicates, as has been noted for micas, augites, hornblendes, olivines, etc., and the separation from augites and hornblendes of calcium silicates) take place rapidly, the union between magnesium and silica is so strong that residual secondary, more or less hydrated, magnesium silicates are encountered at every step. Thus, an investigation of the products of weathering of the augite and hornblende groups usually shows considerable hydration, a great decrease in the CaO content, sometimes to disappearing point, although it may have originally been 10%, and a loss of FeO. There thus remains a hydrated magnesium metasilicate. Another important point is that analyses of the finest fractions of clays (and loams) show the *presence in these of magnesium which is insoluble in hydrochloric acid.*[1] This magnesium apparently does not belong to the exchangeable bases of the adsorption complex, and obviously enters into the composition of those primary or residual magnesian silicates in which it retains its strong union with silica even when in a very fine state of subdivision. Mineralogists have described a whole series of hydrated magnesian silicates of indefinite composition, whose occurrences clearly point to their origin as a result of the weathering of other magnesium silicates, on which they form crusts or films (*zöblitzite, enophite, dermatine, melopsite*).[2]

*Talc* and *serpentine* are frequently referred to this group of residual products, but other workers deny this. The remarks given on kaolinization (p. 87) are not out of place here. We would never consider the talc of certain definite localities, or that more widespread form, talc schist, as a product of weathering. There is no doubt that in these cases neither the conditions of bedding, nor the appearance and structure of the minerals and rocks, resemble those of products of weathering in any way, but, on the contrary, must be ascribed to other agencies, such as juvenile or phreatic solutions. But at the same time we cannot doubt the possi-

1 Cf. L. P. Bielakova, The composition of soil suspensions, etc., *In* Glinka Memorial Volume (Leningrad, 1928).

2 *Handbuch der Mineralchemie,* Herausgb. H. C. Doelter, Bd. II, 1914. Also J. W. Mellor, *loc. cit.,* VI, p. 423.

bility of hydrated magnesium metasilicates of the acid salt type, analogous to talc in their chemical composition, being formed as a result of weathering. The separation of these minerals from the general mass of weathering products is a difficult matter, but they may be expected to be formed in individual localities, although special search and investigations would have to be made. It is also quite possible that among saponites, sepiolites, etc., we may encounter residual products of the weathering of primary minerals. The majority of the members of these little studied groups, however, are apparently synthetic minerals of the crust of weathering (*v. infra*). To the same extent, all that has been said is applicable to *chrysotile, i.e.* a variety of serpentine which is a hydrated magnesium orthosilicate.[1]

The existence of residual products of weathering of the primary silicates of calcium, sodium and potassium of a similar type must be considered possible. This has been confirmed to some extent by the work of K. D. Glinka (see p. 86), and most fully by the recent work of P. A. Zemiatchensky.[2] The usual intermediate stages of the process are not very stable in contrast to the residual magnesian silicates. Secondary minerals derived from soda-lime silicates, do exist, but their genesis, appearance and chemical nature provide no basis for analogous residual products of weathering.

It is appropriate to give at this juncture some explanation of the so-called *soil-zeolite theory*, which is unfortunately not yet forgotten. Among the aluminosilicates there is an isolated group of minerals known to mineralogists as *zeolites* (*apophyllite, analcime, chabasite, gmelinite, phillipsite, stilbite,* etc.). The group consists for the most part of lime-soda aluminosilicates; potassium may occasionally be present and still more rarely barium (*harmotome*), but neither magnesian nor iron zeolites are known, and in this way they are similar to the feldspar group. The occurrence of these minerals is closely connected with igneous, and especially extrusive rocks (basalts, porphyrites, phonolites,

[1] Another variety of serpentine, *antigorite,* is regarded by some petrographers as a primary juvenile mineral.

[2] *Trans. Dokuchaiev Soil Inst.,* 1933, **8**, pt. 1.

lavas), with contact zones, ore veins, etc. All these minerals owe their origin to post-volcanic processes, and especially to the action of hot solutions on the minerals of the rocks enumerated. In appearance these minerals are usually beautifully formed crystals. It is sufficient only to see a piece of some or other basalt or phonolite with beautiful crystals of zeolites to be dissuaded from any thought that these could have resulted from weathering, and in addition they themselves, on weathering, break down very readily, and in contrast to magnesian silicates, are extremely unstable. But the most important property of these minerals is their peculiar adsorptive power.

Zeolites always contain a certain quantity of water, which they can easily give up and just as easily adsorb again. But it appears that zeolites, freed of water, may again with rapidity adsorb, together with water, the most diverse compounds, such as ammonia, carbonic acid, hydrogen sulphide, ethyl alcohol, dyestuffs, silicon fluoride, etc. It is this property of zeolites which resembles to some extent the adsorptive power of soils and led in its time to the *soil-zeolite hypothesis,* according to which zeolites are formed in the soil by weathering and give it its adsorptive power. As a result there came into use various derivative terms: "zeolitic part of the soil," which was applied to the mineral matter that was dissolved by 10% hydrochloric acid; the "zeolitic adsorption complex" (in contrast to the organic), and so on; and the soil workers, agronomists and foresters who used these terms did not always think of the existence of the true zeolites and of the origin of the term in soil science. At the present time the classic work of K. K. Gedroiz, G. Wiegner and others has cleared up the nature of the adsorptive power of the soil, and shown its direct connexion with colloids and certain of their properties that were, much earlier, partly explained by Van Bemmelen. The soil-zeolite theory has been relegated to the region of history, and even the terms, well established in their time, "soil zeolites," and "zeolitic adsorption complex," are more and more rarely encountered in current literature, and are replaced by more rational terms (aluminosilicic, mineral,

silicic adsorption complex). The very marked part played by magnesium in the phenomena of adsorption by soil colloids sharply emphasizes the failure of the soil-zeolite theory. For the zone of weathering, the group of zeolites are thus primary minerals, which not only do not hinder the weathering of lime-soda aluminosilicates and the solution of calcium and sodium, but actually increase it.

Thus the first stages of weathering are distinguished by the rapid decomposition of calcium silicates in comparison with certain much more stable forms of the double sodium and calcium silicates and especially those of magnesium. But the further distinction between the compounds of these elements depends on the properties of their solutions and subsequent forms.

### 3. The Absorption of Na, K, Ca, Mg From Solutions by Organisms

The diverse ways in which the alkali and alkaline earth metals can be removed from the solutions circulating in the crust of weathering may be divided into three main types: (1) removal by organisms, (2) adsorption by the colloidal complex, and (3) precipitation as salts which have reached their maximum concentration in solutions.

We shall commence with the first. Analyses of both animal and vegetable organisms show the presence of all four elements. Plant physiologists regard three—Ca, Mg and K—as being organogens, whilst in the physiology of animals the fourth, Na, is added. The removal of nutrients by the roots of higher plants is governed by the laws of diffusion and osmosis, and between the solution, the plant absorbent, and the exterior, there ought to exist the quantitative relationships required by these laws. This explains why it is possible for all substances dissolved in natural solutions to permeate the plant organism, whether or no they are necessary for the fulfilment of some or other physiological function. At the same time, however, we observe in plants an ability to select certain definite elements, and as a result the quantitative relationship between the elements absorbed in no way corresponds to that obtain-

ing in the solution from which the absorption was made. The mechanism of the "selective power" of the plant apparently consists in the following: the elements which are required for its development enter into various reactions inside the organism and form new insoluble organo-mineral compounds. Being removed from solution in this way they set free a place for new ions of the same element from the outer solution.

It follows that this selective power affects most strongly those elements that enter into the composition of the various kinds of compounds built up in the life processes of the vegetable organism (*e.g.* chlorophyll, proteins, various enzymes, etc.). We know that, in general, different plants show different selective powers, examples of which have already been given, but there are elements for which the great majority of plants, if not all, show an especially high selective power, and potassium is one of these. In Tables II-V are given the contents of $K_2O$, CaO and MgO in the grain, stems (straw), tubers, roots and tops, of various cultivated plants.[1]

TABLE II.

| 10 kg. dried grain contain in grams. | | | |
|---|---|---|---|
| Plant | $K_2O$ | CaO | MgO |
| Wheat ... | 61 | 6 | 22 |
| Rye ... | 65 | 5 | 19 |
| Oats ... | 51 | 10 | 18 |
| Barley ... | 52 | 5 | 18 |
| Maize ... | 42 | 3 | 18 |
| Buckwheat | 32 | 10 | 29 |
| Mustard ... | 114 | 12 | 19 |
| Beans ... | 152 | 15 | 20 |
| Flax ... | 113 | 27 | 42 |
| Hemp ... | 107 | 113 | 27 |

TABLE III.

| 10 kg. dried stems contain in grams. | | | |
|---|---|---|---|
| Plant | $K_2O$ | CaO | MgO |
| Wheat ... | 73 | 26 | 11 |
| Rye ... | 92 | 36 | 13 |
| Oats ... | 104 | 36 | 18 |
| Barley ... | 110 | 33 | 11 |
| Maize ... | 117 | 50 | 26 |
| Buckwheat | 260 | 191 | 89 |
| Mustard ... | 117 | 186 | 38 |
| Beans ... | 226 | 135 | 30 |
| Flax ... | 110 | 83 | 23 |
| Hemp ... | 54 | 122 | 27 |

A simple comparison of these figures clearly shows the preferential absorption of potash by plants from natural

[1] Data from S. P. Kravkov, T.-b. of General Agriculture, 1930 (Russ.). *Cf. Bull.* 156b. Data on composition of farm foodstuffs, etc., Univ., Leeds, 1936.

solutions, an absorption which so much exceeds that of the other elements that it is hardly possible to find any natural solution with the same ratios between the elements. Of all the examples given we find only two exceptions: these are

TABLE IV.

| 10 kg. dried roots and tubers contain in grams | | | |
|---|---|---|---|
| Plant | $K_2O$ | CaO | MgO |
| Sugar Beet | 213 | 5 | 7 |
| Carrots ... | 196 | 9 | 5 |
| Potatoes... | 228 | 2 | 4 |

TABLE V.

| 10 kg dried tops contain in grams. | | | |
|---|---|---|---|
| Plant | $K_2O$ | CaO | MgO |
| Sugar Beet | 501 | 36 | 33 |
| Carrots ... | 152 | 86 | 12 |
| Potatoes... | 187 | 50 | 27 |

the vegetative organs of mustard and hemp, in which calcium exceeds potassium. Actually, there are no doubt other exceptions, and it may be mentioned that in the wood of pine, and the bark of oak, calcium also predominates over potassium, although in pine needles, oak leaves, and the seed of both trees potassium is predominant. These exceptions, however, which concern only the ratio to calcium, do not alter the definite conclusion that an immense quantity of potassium, in contrast to the other alkali and alkaline earth metals, is absorbed by plants and thus held in the crust of weathering. If we remember that the total quantity of potash in the primary rocks of the earth's crust is smaller than that of calcium, then the relative amount of potash taken up by plants is still more significant. The forms assumed by potassium in the organism are apparently fairly diverse. The part played by potash in the molecule of plant proteins may be taken as fairly certain; its part in the structure of blood vessels in higher vertebrate animals has been fully demonstrated, and the potash salts of various organic acids exist in plant organisms. But this hardly exhausts all the forms of its compounds. Potassium is alleged to play a certain part in the formation of carbohydrates, *i.e.* in the processes of photosynthesis, although it is also necessary for plants that do not carry out photosynthesis, *e.g.* lower

fungi and bacteria. It is now apparent that, while the sodium in primary rocks passes through a considerable part of its cycle and enters the hydrosphere in the dissolved state, about 60% of the potassium remains in the products of weathering unleached by water. This is largely the potassium held by land organisms, but partly that of the primary minerals that are resistant to weathering (*e.g.* microcline).

To some extent the data that we have given for calcium and magnesium show fairly clearly the greater selective power of plants for magnesium. Even in those cases where the calcium content exceeds that of magnesium, their ratio is decidedly different from that in natural (soil) solutions, in which the excess of calcium over magnesium is considerably greater. Of all the examples only the Ca/Mg ratios for the stems of beans, hemp, and the roots of carrots approximate to those of the natural solutions. There are a few cases in which magnesium exceeds calcium, but this is an extremely rare occurrence in soil solutions. Thus, plants must take up the magnesium necessary for their growth, and the mechanism of this selection appears to be primarily connected with the formation of chlorophyll, in which magnesium plays a part similar to that of iron in haemoglobin. This, however, does not restrict the rôle of magnesium, which seems to be necessary also for non-chlorophyll plants and for animals, in whose organisms it has something to do with the blood-forming processes.

As regards calcium, it might at first sight be thought that it is taken up by plants only because of its abundance in natural solutions. Although many lower plants (fungi and bacteria) may dispense with calcium, experiments with green plants have demonstrated the necessity of calcium in their mineral food. Analyses of these plants show that calcium, in contrast to potassium and magnesium, is accumulated, for the most part, in the vegetative organs: stems, woody tissue, bark, etc. It has a neutralizing effect on the organic acids in plant organs, forming salts (*e.g.* calcium oxalate). But, in addition, individual investigations show that it has a more important part in the assimilation of car-

bon, the transfer of proteins and the formation of enzymes. Until recently, however, it was not clear to what extent calcium played a *specific part, i.e.* was irreplaceable by any other element. It now appears that calcium exercises a specific protective action. Experiments show that in the absence, or insufficiency, of calcium, solutions of certain nutrient salts, in particular of magnesium, have a poisonous effect on plants.[1] Taking into consideration the fact that calcium frequently forms a substantial part of various tissues and organs of land animals (bony tissue of vertebrates, shells of land molluscs, shells of eggs, etc.), we see that part of it is held in the subaerial crust of weathering not only by plant, but also by animal organisms.

Turning now to sodium, it should be remarked that, although botanists do not consider it to be an organogen, its content in plants frequently exceeds that of calcium, and this occurs even when calcium definitely predominates over sodium in the soil solution. Thus, we find the following data: garlic contains per 100 gm. dry matter, 110 mg. $Na_2O$, and 80 mg. CaO; lentils, 243 mg. $Na_2O$ and 114 mg. CaO; carrots, 115 mg. $Na_2O$ and 83 mg. CaO. In this way sodium may in certain cases be *actively* absorbed by plants; in other words, it is utilized by them for internal reactions in which it possibly plays a part similar to that of other elements and may partially replace them. Sodium is also absorbed by the animals inhabiting the land. In the higher vertebrates it is found in the composition of all tissues and in the blood. There is no doubt, however, that both the absolute and the relative amounts of sodium taken up by land organisms in a definite interval of time is considerably less than those of the other elements we have considered. We thus see that all these elements are absorbed by land organisms, but in very variable amounts. Potassium, in this connexion, occupies the first place, and it apparently is one of the characteristic elements of that part of the biosphere which occupies the land.

[1] Recent investigations by the late K. K. Gedroiz showed, however, that strontium may replace calcium in the mineral nutrients of plants. *Cf.* Udobrenie i Urozhai, 1930, No. 6.

Up to the present we have only considered those forms of the absorption of elements by organisms that take place on land, *i.e.* before the solutions enter rivers and marine basins. But when they enter seas and oceans these elements again meet many consumers in the form of marine animals and plants. A little earlier we calculated that at a certain moment when all the sodium of a certain primary rock mass has reached the hydrosphere and there attained molecular dispersion, over 95% of the calcium, over 50% of the magnesium, and 30% of the potassium of that same mass has been removed from solution in the waters of the ocean. This removal is without a doubt carried out, in the main, by organisms. We see in this case that the principal part among the absorbed elements is taken by calcium. On land it already acts to some extent as a *skeleton* element, being held in the mechanical tissues of organisms, but in the ocean this part is realized to the fullest degree: the great mass of sea animals that construct their skeletons, shells and armour from calcium carbonate build up from these great thicknesses of submarine sediments. In these shelly deposits calcium is joined by magnesium, but in much smaller amounts[1]; the ratio of calcium to magnesium reaches 9 or more, and is rarely less than 5. A considerable part of the magnesium, since it is a necessary element in chlorophyll, is absorbed in the upper part of the hydrosphere by chlorophyll-bearing phytoplankton. And here, of course, the organisms also absorb potassium, and to a much less extent sodium.

## 4. The Adsorption of Ca, Mg, K and Na by Adsorption Systems

Between the solutions circulating in the crust of weathering and the elements of the solid phase there inevitably occur interactions, among which the physico-chemical adsorption of the cations of dissolved salts is especially important. This process is characteristic of the colloidal

[1] The high content of $MgCO_3$ in certain calcareous rocks (coral limestones) is explained by the enrichment with magnesium from sea water subsequent to their deposition.

particles of weathered rocks and soils (*i.e.* particles of diameter less than $0{\cdot}1\mu$), but takes place to some extent with particles of greater size. It is well known that, adsorbed alike by the organic and the mineral adsorption complex, the cations are able to displace and replace each other, but at the same time they have quite different *energies of adsorption,* or, more correctly, *energies of entry into the adsorption complex.* In particular, investigations have shown that for the elements we are interested in the following series holds good:—

$$Ca^{\cdot\cdot} > Mg^{\cdot\cdot} > K^{\cdot} > Na^{\cdot},$$

*i.e.* under similar conditions (the same concentration in solution) calcium will be adsorbed more rapidly and to a greater extent than magnesium, magnesium more than potassium, and that more than sodium, whilst the hydrogen ion enters most easily of all.

These facts, well established both theoretically and experimentally, are clearly supported in natural compounds. Thus, the adsorption complex in which *calcium* predominates is the most common in the upper part of the crust of weathering. Adsorbed calcium is found in all soils of tropical and temperate climates, forest, steppe or desert. It occurs in the boulder clays and varve clays of the glaciated regions, the red soils of the Caucasus, not to mention the loess and loess-like loams. Recent investigations by K. K. Gedroiz show that the presence of adsorbed calcium is characteristic of every layer in the subaerial crust of weathering that is occupied by roots, being a necessary condition for the existence of plants feeding through their roots.[1] This wide, one might almost say universal, distribution of adsorbed calcium agrees well with the low resistance of calcium minerals to weathering, its customary presence in the natural solutions of the crust of weathering, and its great ease of entry into the adsorption complex. As we have already remarked, hydrogen is still more easily adsorbed, but natural solutions with a high hydrogen ion concentration are not of such *universal* distribution as solutions of salts, and, above all, of calcium bicarbonate. Neverthe-

[1] *Loc. cit.*

less, regions in which acid solutions are active, occupy a fairly large part of the crust of weathering, and in these regions the adsorption complex contains, in addition to calcium, hydrogen, which may sometimes even predominate. The fundamental types of the commonest adsorption compounds in the crust of weathering are:—

I. $[SiAl \ldots 2nOH']nCa^{\cdot\cdot}(nMg^{\cdot\cdot}, 2nK^{\cdot}, 2nNa^{\cdot})$.

II. $[SiAl \ldots 2nOH']2nH^{\cdot}(nCa^{\cdot\cdot}, nMg^{\cdot\cdot})$.

The first is a mineral adsorption complex, saturated for the most part with calcium, but containing some magnesium, and a very small amount of the alkali cations. We meet this complex over the great areas of the steppe, where it only yields place to other systems in regions of intense salinization; but of that we shall have more to say shortly. The mineral complex, saturated with calcium, is accompanied by an organic complex similarly saturated with calcium and magnesium. It is obvious that the accumulation of these calcium humates can only occur where a more or less considerable amount of humus is formed. In contrast, the loose crust of weathering in regions of moist climate is leached to a considerable extent, and the adsorption complex contains a certain amount of exchangeable hydrogen. In this case, too, calcium usually predominates (by weight), but when the figures are recalculated in equivalents, hydrogen frequently gives higher, sometimes considerably higher, values.

Calcium, however, is present in all these compounds, and we may say that the *seat of origin of adsorption systems containing calcium is the crust of the weathering of the entire earth*. It would, however, be incorrect to affirm that this calcium system is quite stable. It is true that it is more stable than adsorption systems containing sodium, for example, but less so than a mineral adsorption complex containing mostly magnesium (*vide infra*).

The wide distribution of complexes, saturated with calcium, is explained not so much by the stability of such systems as by the fact that in the calcium cycle these systems form

a characteristic, and almost inevitable, phase through which the bulk of the calcium passes. From the organic adsorption complex on decomposition (aerobic) calcium separates in the form of carbonate, and from the mineral complex Ca is easily taken up by organisms, but it must be assumed that a certain part of the adsorbed calcium quits the zone of weathering in sedimentary rocks for the deeper shells of the earth's crust.

In determinations of the composition of the exchangeable bases in the soil it is frequently found that the alkali metals are present; but in such extremely small amounts, especially of potassium, that their accurate determination by ordinary chemical methods is not easy. Considering the smaller energies of adsorption of the alkali bases in comparison with that of calcium, the greater resistance to weathering of primary alkali aluminosilicates in comparison with calcium silicates, and therefore the greater amount of the latter metal in the natural solutions circulating among the aluminosilicate country rocks, the relations between the adsorbed alkalis and calcium become clear, and we are making no great error when we omit the adsorbed alkalis from the second type of adsorption complex—the type characteristic of the regions in which the crust of weathering is strongly leached.

In certain cases that occur in regions with an abundance of easily soluble sodium salts in the drifts and soils (NaCl, $Na_2SO_4$, $Na_2CO_3$), we find that both the mineral and the organic adsorption complexes contain a marked amount of exchangeable sodium :—

$$[SiAl \ldots 2nOH']2nNa^{\cdot}.$$

This adsorption compound is very highly dispersed, and is an extremely unstable system. Its breakdown in certain cases is shown very graphically, and there is no reason to expect crystalline products of this adsorption system in its undecomposed form in the crust of weathering.

### 5. Isomorphism of Magnesium and Iron

The cases in which the main content of the adsorption system is exchangeable magnesium are of a different charac-

ter. We have already remarked on the great chemical stability of magnesian silicates—more accurately, the stability in these silicates of the union between magnesium and silicon (p. 73). It is rather striking that the same sort of thing is observed in adsorption systems containing replaceable magnesium. Although it yields place to calcium in its *energy of entry* into the adsorption complex, magnesium greatly exceeds calcium in the strength with which it is held in the adsorbed state. This makes its removal from the adsorbed state by other cations extremely difficult.[1] The formation in nature of adsorption systems in which adsorbed magnesium predominates is associated with definite conditions. Let us suppose that the products of the weathering of some or other complex rock undergo energetic leaching by great quantities of carbonated water. To begin with, the leaching solution will contain mostly calcium bicarbonate, the product of the most easily weathered lime minerals. Therefore the adsorption complex will be largely saturated with calcium. During subsequent action, when the calcium minerals have been to a great extent decomposed, the solution will acquire the bases from the more stable alkali aluminosilicates and magnesium silicates. Then magnesium will to some extent remove the calcium from the adsorbed state and be adsorbed to a greater extent than the alkalis.

Further, if we suppose the complete or almost complete disintegration of silicates, the hydrogen ions in the $CO_2$-water will act almost alone. This leads to a still greater relative enrichment of the adsorption complex with magnesium, since the hydrogen will replace calcium easier than it will magnesium. We obtain, in this way, an aluminosilicic,

[1] In his recent address to the III International Congress of Soil Science the late Prof. Wiegner retracted his former views, and on the basis of new experiments concluded that magnesium is removed more easily than calcium, strontium and barium. These experiments were carried out with permutit and clay, freshly treated with divalent cations. In the colloidal complex of the crust of weathering, however, in addition to truly adsorbed magnesium, there is to be found magnesium which is still part of the undisturbed crystal lattice (W. P. Kelley, W. M. Dore and E. M. Brown, *Soil Sci.*, 1931, **31**, 25-55) and magnesium, which through the aging of the complex, has left the truly adsorbed state to assume a definite position in the lattice (C. E. Marshall and R. S. Gupta, *J. Soc. Chem. Ind.*, 1933, **52**, p. 433). Such magnesium, we may assume, is more difficult to replace than truly adsorbed magnesium.

or ferrisilicic complex saturated mainly with *magnesium* and *hydrogen, i.e.* somewhat analogous to the hydrated silicates or aluminosilicates of magnesium. $CO_2$-water has an acid reaction and will up to a point dissolve out iron in the form of carbonate, and, consequently, will contain a certain amount of Fe'' ions, which may be adsorbed at the same time as magnesium and hydrogen. It is obvious, also, that in this system there may be a certain amount of the calcium previously adsorbed.

Such phenomena are observed by soil workers in the so-called ortstein horizons characteristic of certain soils formed under cool moist climate.[1] It is possible that they also occur on a greater scale in still deeper horizons of the crust of weathering, but little investigation has been made. In ortstein horizons the adsorption complex is built up of complex coagels of silica, hydrated ferric oxide, alumina, and organic matter (humates), from which the latter sooner or later disappear and we are left with a system analogous to the hydrated ferro-magnesian silicates, aluminosilicates and ferrisilicates. We may take it as proven that this analogy explains not only the coincidence of both adsorption compounds and crystalline minerals among its components, but also, in a certain group of cases, the genetic relationship between the adsorption compounds and the crystalline minerals into which these systems pass in course of time. The formation, for example, of such crystalline minerals as *paligorskites* and *xylotiles* at the expense of the adsorption systems, as has been shown (p. 112), may be considered as having been proved after it was found possible to follow this transformation in a series of microscope slides made from active and relict ortstein horizons.[2] We can hardly doubt that among other of the innumerable hydrated magnesium

[1] *Cf. Ann. Geol. Min. Russ.*, vol. XIV, pt. 9, pp. 273-276.

[2] The first communication on the occurrence of *paligorskite* in soils (*Ann. Dokuchaiev Soil Com.*, 1915, pt. 2, pp. 125-138) gave rise to the not quite correct conclusion that I found paligorskite in podzolized soils (K. D. Glinka, *T.-b. of Soil Science*, 2nd Ed.). The mineral was actually found in the relict ortstein horizons of present-day steppe soils as described in greater detail in my larger work on the Don sands (*Trans. Dokuchaiev Soil Inst.*, 1926, vol. 1, and 1927, vol. 2). It is difficult to conceive of conditions in ortstein horizons still in formation that would be suitable for the crystallization of the complex adsorption systems formed there.

silicates there occur not only the alteration products of primary minerals but also products of the crystallization of adsorption systems (Chap. III, p. 106, Sect. 12), and *we may assume that the isomorphism of magnesium and iron in these minerals is due to processes in the crust of weathering.*

In this way the alkali, and alkaline earth, metals form four categories of typical adsorption systems within the crust of weathering. The occurrence of the one characterized by the predominance, or considerable participation, of sodium is bound up with specific saline conditions, and is, apparently, rapidly disintegrated even within the crust of weathering. The others contain exchangeable calcium and hydrogen for the most part, but magnesium may predominate. These are the most widespread, and are the forms in which these bases may leave the zone of weathering in sedimentary rocks for further transformations in the deeper shells. In many cases, however, the adsorption compounds containing magnesium, as we have seen, may crystallize even within the zone of weathering. But while these compounds are in the crust of weathering, and especially in its uppermost parts, their exchangeable bases may be taken up by plant roots[1] and replaced by other cations with the formation of new salts. Thus, for example, in certain areas of the crust of weathering an extremely characteristic process is the formation of gypsum at the expense of calcium removed from the absorbed state :—

$$[SiAl \ldots 2nOH']nCa'' + nNa_2SO_4 \rightleftharpoons$$
$$[SiAl \ldots 2nOH']2nNa' + nCaSO_4.$$

Under the conditions of subaerial weathering, as has already been remarked, we do not find adsorption systems with a very marked content of exchangeable potassium, but on the sea-bottom the formation of the ferrisilicate glauconite (p. 110) may be regarded as due to the crystallization of adsorption systems in which no small place is held by potassium among the replaceable bases.

[1] It should be noted that plant roots exude solutions of an acid nature which must react with the adsorbed bases, replacing them with hydrogen, and so facilitating their intake by the plant.

## 6. The Separation of Bases from Solution in the Form of Lacustrine Salts, and the Salts Permeating Clastic Rocks and Sediments

Passing into solution during weathering and the decomposition of organic residues in the form of sulphates, chlorides, borates and other easily soluble salts, the alkalis and alkaline earths may again separate out from these solutions within the zone of weathering when their concentration exceeds a certain value. The various cases may be divided into two groups: (1) separation in the form of lacustrine (chemical) deposits, and (2) separation in the form of "ground" salts, *i.e.* salts permeating sediments, drifts and the products of weathering. The first group is connected with the formation of the so-called salt lakes by the permanent or periodic accumulation, in closed basins or ponds, of water containing dissolved salts, or by the isolation of marine estuaries. The separation of chemical sediments is due to the evaporation being in excess of the amount of water entering from the catchment basin or from the sea (*e.g.* Karabugaz). It is evident that under such conditions the concentration of dissolved salts ought gradually to increase and the salts to separate from solution in the order of their relative solubilities, beginning with the least soluble.[1] The mineralogical composition of the separated salts is of great variety, and depends both on the temperature at which separation takes place, and on the nature and origin of the salt lake. Among the minerals are the simple salts of hydrochloric, sulphuric, carbonic and other acids, together with innumerable double salts, hydrated and anhydrous. The commonest include: *rock salt* $NaCl$, *mirabilite* $Na_2SO_4.10H_2O$, *thenardite* $Na_2SO_4$, *gypsum* $CaSO_4.2H_2O$, *anhydrite* $CaSO_4$, *epsomite* $MgCl_2.7H_2O$, *kieserite* $MgSO_4.H_2O$, *glauberite* $Na_2SO_4.CaSO_4$, *astrakhanite* $Na_2SO_4.MgSO_4.4H_2O$, *thermonatrite* $Na_2CO_3.H_2O$, *trona* $Na_2CO_3.NaHCO_3.2H_2O$, *gaylussite* $CaCO_3.Na_2CO_3$.

[1] It is evident that inasmuch as we are dealing with the chlorides and sulphates of the alkalis and other easily soluble salts the deposits cannot be described as of *marine origin*. This was fully established by Van't Hoff in his classic work on the Stassfurt salt deposits, which are typical lacustrine sediments.

$5H_2O$, *lacustrine dolomite* $CaMg(CO_3)_2$, *tincal* (borax) $Na_2B_4O_7.10H_2O$; of the potassium salts in lacustrine deposits there occur *sylvite* KCl, *carnallite* $KCl.MgCl_2.6H_2O$, *kainite* $KCl.MgSO_4.3H_2O$, etc. We shall discuss the distribution and types of these lakes when we consider the distribution of products of weathering. The deposits of salt lakes may, within the crust of weathering, undergo desalinization to some extent, or may be buried with sedimentary rocks in the deeper zones of the earth's crust and there undergo further alteration.

Although the deposits of salt lakes have been studied in great detail from both the mineralogical and the physico-chemical aspects, the same cannot be said of the formations arising from "ground" salinization. The process of salinization itself takes place at the expense of the solutions circulating through drifts, sediments, and the products of weathering, in the form of permanent, or periodic, horizons and streams of ground (soil) water. In certain places atmospheric precipitation seeps through to the ground water and enriches it with the products of weathering that are dissolved on the way, while in other areas the reverse process takes place: the ground water diffuses both above and below the water-bearing layer through capillaries and in films covering individual grains and particles; on its way it evaporates, and the dissolved salts separate out and enrich both layers of the drift. It is just in this way, as we shall see later (p. 182), that the enrichment of loess and similar deposits with calcium carbonate occurred and is still taking place. In many localities the salinization of the soil and subsoil by chlorides and sulphates takes place in the same way. Surface (soil) chloride-sulphate solonchaks form a particular example of this type.

Direct analyses of such soils and subsoils show that sodium salts play the greatest part in the salinization, calcium and magnesium to a much less extent. With sufficient accuracy we may assume that the salts present are sodium chloride and sodium and calcium sulphates. There are cases where we find $CaCl_2$ and $MgCl_2$ also, and may suppose the presence of $Na_2CO_3$, but just as to which mineral individuals

these salts separate in the subsoil, with what admixtures and on what depends the great diversity of their outward forms, we up to the present do not know. These formations have not been studied mineralogically, even those varieties, which are not diffused throughout the mass and invisible to the eye, but which form clearly isolated nodules, concretions, crusts, earthy masses, etc. These alkali, and alkaline earth salts permeating continental deposits (sediments) become redistributed, react with one another and with other compounds in the soil, in particular with the adsorption complex. They nourish specific organisms, such as the solonchak grasses and shrubs, and apparently a peculiar microflora, and give rise, as we shall see below, to just as singular land forms in which there exists a regular interdependence (but by no means an equilibrium) between the saline subsoil, salt lakes, and the corresponding regions of the biosphere.

### 7. The Compounds of Barium, Strontium, Copper, Silver, Zinc and Mercury, in the Crust of Weathering

We have just considered the changes undergone by the commonest alkalis and alkaline earths. These changes are to some extent analogous to those undergone by the rarer members of these groups, *e.g.* barium and strontium, among whose vadose compounds we encounter both carbonates and sulphates: *barytes* $BaSO_4$, *witherite* $BaCO_3$, *celestite* $SrSO_4$, *strontianite* $SrCO_3$. As for the other metallic elements of these groups: lithium, rubidium, cæsium, copper, silver, gold, zinc, cadmium, mercury, we can say very little about their rôle in the crust of weathering in the present state of our knowledge. Certain compounds of lithium, rubidium and cæsium are known—minerals indubitably of the deeper sheaths of the earth's crust, such as *lithium mica* (*lepidolite*) in which is found an isomorphous admixture of rubidium and cæsium, or *pollucite*—an extremely rare cæsium silicate. In the upper sheaths, including the crust of weathering, these compounds are apparently decomposed, and the elements are found in the dispersed state only and do not give molecular chemical compounds. The primary compounds of copper, silver, zinc and mercury occurring in

the crust of weathering are mostly sulphur compounds: *chalcopyrite* $CuFeS_2$, *bornite* $Cu_3FeS_3$ (or $Cu_5FeS_4$), *argentite* $Ag_2S$, *zinc blende* ZnS, *cinnabar* HgS. There is also a whole series of vadose minerals formed for the most part in the upper parts of metalliferous veins which penetrate the crust of weathering. Such are native copper, silver and mercury, the oxides, sulphates, and carbonates of copper and zinc, *e.g. cuprite* $Cu_2O$, *tenorite* CuO, *chalcanthite* $CuSO_4.5H_2O$, *malachite* $CuCO_3.Cu(OH)_2$, *azurite* $2CuCO_3.Cu(OH)_2$, *zincite* ZnO, *zinc sulphate* $ZnSO_4$, *smithsonite* $ZnCO_3$, etc.; for silver the vadose halogen compounds: *embolite* AgCl(Br), *cerargyrite* AgCl, *bromyrite* AgBr, *iodyrite* AgI.

There is no doubt that quite significant amounts of zinc and copper, during their cycles in the crust of weathering, pass through living matter, being absorbed by organisms not just passively from solution, but becoming part of organometallic compounds and fulfilling some or other physiological function. Thus, copper is combined in the organic compound *hæmocyanine,* the blood pigment of certain lower animals like molluscs and *Arthropoda.* Zinc has been found in the blood of the molluscs *Sycotypus canaliculatus* and *Fulgur curica,* and a considerable part of it is combined in organic compounds. Both copper and zinc are concentrated in the liver, blood and muscle of a number of invertebrates (*Cœlenterata, Echinodermata,* nematoids, crustacea, molluscs), and are found in the liver, muscle, skin, milk glands, the seminal and other organs of higher vertebrate animals. Certain experiments have been made to show the necessity of these elements to organisms. Thus, it has been observed that mice which do not receive zinc in their food do not live so long as those which do receive it.[1]

Native gold and a number of other noble metals (p. 42) are not oxidized in the zone of weathering and give rise to no compounds. Cadmium to a considerable extent follows zinc.

It is not out of place here to mention lead, which in many respects resembles zinc in its reactions in the zone of

1 Vinogradov. *Priroda* (Russ.), 1928, No. 1.

weathering. It appears largely as the sulphide *galena* (PbS), in admixture with pyrites and sphalerite, which can be oxidized into the vadose sulphate—*anglesite* ($PbSO_4$) or converted into the carbonate *cerussite* ($PbCO_3$) and much more rarely into native lead.

## 8. The Manganese Cycle

Of the remaining elements which in some or other of their compounds act as a metal, manganese deserves careful consideration, since, in spite of the small amount of it in the earth's crust (0·1%), it plays an important part in both the zone of weathering and the biosphere. According to Washington it is present in igneous rocks to the extent of 0·124%, its content in sedimentary rocks, sandstones and shales amounts to no more than traces, but in limestones it may reach 0.05%. Among the juvenile and phreatic manganese minerals that are primary for the crust of weathering are the following: *wolframites,* such as *hübnerite* $MnWO_4$; *niobates: columbite* $(Fe,Mn)Nb_2O_6$; *tantalates: tantalite* $(Fe,Mn)Ta_2O_6$; *aluminosilicates,* especially the group of *garnets* (*spessartite* $Mn_3Al_2Si_3O_{12}$); *silicates: rhodonite* $MnSiO_3$; *orthosilicates: helvine* $(Mn,Fe)_2(Mn_2S)Be_3(SiO_4)_3$, *tephroite* $Mn_2SiO_4$; *titanosilicates* to which belongs *astrophyllite;* oxides: *manganosite* MnO, *hausmannite* $Mn_3O_4$, *braunite* $3Mn_2O_3.MnSiO_3$. In addition, manganese compounds occur isomorphously in many silicates (hornblende), aluminosilicates, aluminoborosilicates, ferrisilicates, ferrites, aluminates and other juvenile and phreatic minerals. In the great majority of the compounds enumerated manganese acts as a divalent base to different acids, and this form is characteristic of juvenile minerals. Trivalent manganese which comes in with the sesquioxides is less common than the others, but it seems to occur in certain aluminosilicates, for example, in garnets, and perhaps in ferrisilicates. *Braunite* may be regarded as a manganese salt of manganous acid $H_2MnO_3$ in isomorphous mixture with the metasilicate $MnSiO_3$. In this case manganese is present both as a divalent metal and a tetravalent metalloid. *Hausmannite* is the manganese salt of orthomanganous acid ($Mn_2MnO_4$).

Thus, the anhydride of both acids is $MnO_2$, which is the highest state of oxidation in which manganese is found naturally. It is necessary to note that compounds of manganese in the highest state of oxidation are commonest in the zone of weathering, and if we observe them in braunite and hausmannite, *i.e.* phreatic minerals according to Vernadsky, it is simply because these minerals are characteristic of the upper part of the phreatic region, *i.e.* that part which is the transition to the zone of weathering.

On the disintegration of juvenile and phreatic manganese minerals, the metal goes into solution either in the form of a sol or as bicarbonate; the latter is only maintained in solution, as with ferrous bicarbonate, by the presence of free carbon dioxide. As regards the sol state, the conditions necessary for it, just as for the separation of gels of manganese oxide and its coagels with silica, organic colloids, sesquioxides, and in particular with ferric oxide, are extremely diverse. This can be explained first of all by the chemical nature of manganese and its ability when in the disperse phase to change its charge readily with change in conditions, and with that the conditions of equilibrium. Innumerable cases of the separation from the dispersed phase of gels and coagels of manganese compounds are known, both in the subaerial crust of weathering and on the sea-bottom. On land in the region of moist tropical and temperate climates, the development of podzolized soils leads to the formation of a great many varieties of *pea ore* and *ortstein* by manganese and iron, and in the ortstein there is also a possibility of coagels of these hydrated oxides with silica. Its concomitant accumulation with iron is also known in limonite, lacustrine and bog ores, in which it occasionally predominates over the iron. Especially great accumulations of hydrogels of manganic oxide are found on the sea-bottom, together with varying amounts of hydrated ferric oxide, and often the manganese is greatly in excess of iron and other admixtures (*e.g.* up to 70% $MnO_2$, more than 7% MnO, more than 10% $H_2O$). These formations appear as large concretions, small nodules, and coatings on shells, bones, blocks of rock, all of which go by the name of *wads* and are

especially characteristic for the sea-bottom of the deep areas of the Pacific, Indian, Atlantic, and Arctic oceans, and are found in large quantities in the Baltic, Barents and Kara Seas; they are also found in the Black Sea and others. Occurring in the shallow-water deposits also, the wads here usually contain more iron.

The predominance of manganese over iron in many wads, including the deep-water accumulations, is explained fairly satisfactorily by the fact that, during the *slow oxidation* of solutions of iron and manganese carbonates, iron is more rapidly precipitated as hydrated ferric oxide, whereas manganese is retained longer as carbonate and consequently may be removed farther. This explains the enrichment of deep-sea wads, but no small part in the variation of the ratio between iron and manganese in coagels is played by the complicated conditions of the coagulation of these compounds from the sol state, and these conditions are still not at all clear.

Although the higher oxides of manganese are characteristic of the crust of weathering, that does not mean that the lower ones have no place there. As we have already seen, certain reduction processes are peculiar to and characteristic of the cycles occurring in the crust of weathering (p. 39), and, of course, any oxygen compound of manganese entering the sphere of these processes is easily reduced to a lower state of oxidation. The ability of manganese to yield reversible oxides in the process of oxygen circulation in the crust of weathering has already been mentioned (p. 49). Reduction processes, the presence in vadose solutions of manganese carbonate, the formation of *rhodochrosite* ($MnCO_3$) in the upper parts of ore veins containing manganese minerals and of stalactites of the rare mineral *mallardite* ($MnSO_4$), compel us to refer carbonates and sulphates of manganese to vadose forms, evidently extremely unstable in the crust of weathering. Theoretically, we may assume that manganese can also act as an exchangeable base since we have supposed the possibility of molecular vadose solutions of its salts.

The crystallization of wads, and, in general, of gels of

hydrated manganese oxides leads to the formation of manganese minerals of complex composition, some of which have a simple, yet definite, crystal structure. These forms include *psilomelane*, which is semi-crystalline and of indefinite composition and probably consists of a mixture of $Mn_2O_3$ and $MnO_2$ and their hydrates, and *pyrolusite*, which is crystalline and corresponds to the anhydrous dioxide $MnO_2$. It is quite possible that the above-mentioned *hausmannite* and *braunite* are also products of the crystallization of vadose gels and coagels of oxygen compounds of manganese removed to the zone of metamorphism. In the deeper parts of the phreatic shell, these former gels and coagels give rise to many minerals, including, perhaps, those manganese minerals already enumerated, but the processes are beyond our investigation.

The part played by organisms in the small manganese cycle in the crust of weathering may be of two kinds. The first is indirect, and is expressed by the dependence of manganese carbonates on the evolution of $CO_2$ for their formation and rapid solution in water, whilst the formation of humus results in the formation of coagels with the manganese oxides. In the second manganese acts directly as an organogenic element. The presence of manganese in ashes of plant and animal organisms that live in soil rich in manganese is not in itself proof of an active rôle in the biosphere. Such accumulations may be purely passive. These facts are of interest in another way. Thus, the absorption by plants of manganese from its accumulations in the form of *pyrolusite*, $MnO_2$, is proof that there exist in the soil processes that can convert manganese compounds into more soluble forms.

More eloquent evidence of the active rôle of manganese in living matter is to be found in the higher concentration of the element in the organisms than in the surrounding medium; such concentration as is observed for certain marine algae, lichens, fungi, and other low plants. To this category belongs the part played by the previously-mentioned bacteria of the genus *Crenothrix*, etc. (p. 37) in the processes of oxidation and deposition of manganese in the form of lacustrine

and bog ores and wads. This process, just like the oxidation of iron, is part of the respiration process of these bacteria. In this connexion, the positive effect of manuring with manganese salts on certain cultivated plants might be mentioned. The successful cultivation of tomatoes in certain parts of Florida, for example, was begun only after experiments in the use of manganese fertilizer had succeeded. All this points quite definitely to manganese as an element having an active part in living matter, either as a substitute for some other element (iron ?) or, perhaps, having a specific function of its own. It is also relevant to mention that manganese has been found in the blood pigment of certain lower organisms. In this way we see that the changes undergone by manganese compounds are analogous in many cases to those of iron. Just like the latter, manganese forms easily reversible oxides, and a considerable part of it passes through certain stages in combination with living matter.

### 9. The Chlorine, Bromide and Iodine Cycles

Of the other elements that make up only a small part of the earth's crust, yet are of great importance, chlorine, sulphur and phosphorus deserve special mention. Chlorine, which amounts to only 0·19%, has a whole series of juvenile forms. In volcanic emanations, for example, the presence of $Cl_2$ and HCl has been noted, as has also the separation of chlorides from dry fumaroles: NaCl, $NH_4Cl$ (Icelandic volcanoes). In addition, the action of hot vapours of HCl on rocks forms the chlorides of other metals, such as $FeCl_3$. Chlorine is also present in certain of the minerals of igneous rocks: *chlorapatite* $Ca_5(PO_4)_3Cl$ and *sodalite* $3NaAlSiO_4 . NaCl$. It appears to be present in some rocks in a dispersed state. Finally, in vein formations chlorine is found as *pyromorphite* $Pb_5P_3O_{12}Cl$, *mimetite* $Pb_5As_3O_{12}Cl$, and *vanadinite* $Pb_5V_3O_{12}Cl$.

In igneous rocks chlorine amounts on the average to 0·05%; in certain cases, however, particularly in basic rocks rich in sodalite, its content may reach 0·7%. In sedimentary rocks, on the other hand, it amounts to only 0·01%. But in

spite of those small quantities, its contents in the hydrosphere reaches 2%, and is the most important element in the dissolved matter of the water, amounting to 55%. With fair accuracy we may assume that, at the present time, the hydrosphere contains over 60% of all the chlorine in the earth's crust, and of the remainder about 35% is in igneous rocks.[1]

On weathering, chlorine is leached out of minerals and rocks much quicker than the other elements, and it is always present to some extent in the vadose solutions of the land. In river water its content ranges from 0·5 to 30% of the sum of dissolved matter.

Vadose minerals of chlorine are formed mainly by precipitation from concentrated solution, and predominate in salt lake deposits and among the salts of subsoil salinization. The principal salt is NaCl. Other chlorides have been enumerated above (p. 140). Of the theoretically possible insoluble vadose compounds of chlorine in nature there are encountered those we have already mentioned—*cerargyrite* AgCl, *embolite* AgCl(Br) and *iodobromite*—2Ag(Cl,Br).AgI (p. 143).

The presence of chlorine in organisms naturally depends on its occurrence in vadose solutions, but whether or not it has any specific function in the compounds of living matter we have no clear idea. One thing is quite definite—a considerable part of the chlorine passes through living matter in its cycle.

The fates of the other halogens, bromine and iodine, in the crust of weathering is somewhat different. The most important point is their absence from juvenile minerals; apparently they both occur in a dispersed state in the lower shells of the earth's crust. In sea water iodine is found in quantities ranging from 2 to 0·02 mg. per litre. In salt lakes the quantity is, for obvious reasons, considerably greater, and reaches a few tenths of a gram per litre.

The insignificant iodine content of sea water, quite apart from the small amount of the element in the earth's

[1] It seems that the contemporary distribution of chlorine is a result of its accumulation in the hydrosphere, and it may be assumed that in the earlier stages of the earth's history there was a much higher content in primary rocks.

crust (*c.* 0·0011%), is explained by the fact that it is energetically taken up by marine organisms. Of these accumulators of iodine we may mention specially the brown seaweeds of the *Laminariaceæ* and *Fucaceæ* families, *e.g. L. flexicantis* and *L. claustron* (sea-kale), which are frequently gathered for their iodine in France and Japan, and *Fucus digitatus* and *F. saccharinus* (Scotland). Other weeds noted as accumulating iodine are the *Alaria* and *Potamogetonaceæ* families. The amount of iodine taken up by these organisms reaches comparatively high values. Gautier, who investigated the upper layers of the Mediterranean, found that the iodine there occurs only in the plankton, and not until a depth of 800 m. is reached are iodine compounds found in true solution in the water.[1] In the seaweed iodine takes part in the carbohydrate exchange, and in the deep water forms that are less accessible to light, its content is much higher. Active absorption of iodine has also been observed in certain marine animals (tropical sponges, certain corals and fish).

Iodine is also absorbed, although to a lesser extent, by land organisms. Thus, even in cultivated cereals (wheat, oats, rye) iodine amounts to 0·02 to 0·06 mg. per kilogram of fresh material.[2] The quantity is much greater in halophytes, *i.e.* plants that grow on saline soils, and in these iodine appears to be antagonistic to chlorine and protects the plants from the plasmolysis due to excess chloride.

In general, it can be said that iodine is one of those elements which, although only present in minute quantities, play an extremely important part in the living organism. We know that iodine is largely concentrated in the thyroid gland of the higher animals and is so indispensable that any insufficiency at once brings about diseases such as goitre and cretinism, to which mountain-dwellers are prone. The disease is due to the lack of iodine in the drinking water.[3]

[1] F. W. Clarke, The Data of Geochemistry, 5th Ed., Washington, 1924, p. 122.

[2] *Cf.* Vinogradov. *Priroda* (Russ.), 1927, No. 9. It is obvious that the content expressed as a percentage of fresh material is extremely indefinite.

[3] Recent work suggests that the incidence of goitre may be associated with the occurrence of radioactive substances.

The amounts necessary, however, are of the order of a few thousandth parts of a milligram per litre.

The few vadose iodine-bearing minerals, such as *lautarite* $Ca(IO_3)_2$, a component of Chili saltpetre, and the silver compounds *iodoargyrite* AgI, *cupro-iodoargyrite* (Ag,Cu)I, *iodoembolite* Ag(Br,I,Cl), also owe their formation to the activity of organisms. For lautarite, at any rate, there is no doubt about this; its paragenesis with saltpetre is sufficient evidence. It would appear that vadose accumulations of iodine, when they are buried in sediments and transported to the deeper regions of the lithosphere, become dispersed. Iodine frequently enriches underground waters, appearing in the water of many springs and cases are known in which it is present not only in the form of iodine salts, but also in the form of free iodine.[1]

Bromine, whose content in the earth's crust is considerably greater (0·01%) is found in much greater quantity in sea water (0·007%), and makes up 0·2% of the dissolved salts. Its content in lakes is also greater. Thus, investigations on the Dead Sea showed that at a depth of 300 m. the content of bromine reached 7 mg. per litre of water,[2] and in relation to the total dissolved salts amounted to 2%. In the same way as iodine, bromine is absorbed by organisms, in particular by seaweeds, and forms vadose minerals, certain of which are found among salt-lake deposits: *bromcarnallite* KBr. $MgBr_2.6H_2O$ in which bromine replaces chlorine isomorphously; *brom-bischofite* $Mg(Cl,Br)_2.6H_2O$. In addition to the above-mentioned iodine and bromine minerals, we should mention the insoluble vadose forms: *bromargyrite* AgBr and *embolite* Ag(Cl,Br).

Bromine, which is also encountered in spring water, apparently gives forms analogous to those of iodine in the crust of weathering, but is distinguished, as mentioned above, by its higher content. This last fact makes possible the working of salt lake deposits for the element.[3]

[1] F. W. Clarke, *loc. cit.*, p. 14.
[2] *Ibid.*, p. 171.
[3] Bromine is extracted from the Saksky saline lake in the Crimea.

## 10. Juvenile Compounds of Sulphur and Their Transformations in the Crust of Weathering. Compounds of Selenium and Tellurium

Of much greater complexity and diversity are the changes undergone by the compounds of sulphur. The total sulphur in the earth's crust works out at 0·06% by weight and 0·05% by number of atoms. A great variety of its compounds are met among both juvenile and phreatic minerals. Of the juvenile forms the varieties of native sulphur of volcanic origin must first be mentioned. These are usually found among the sublimates in the craters of active volcanoes.

This juvenile sulphur is usually contaminated with selenium (volcano on the Lipari Islands), tellurium (Japanese volcanoes), arsenic and other elements.

A certain amount of native sulphur in the region of active volcanoes may, apparently, be formed not by direct sublimation, but as a result of the incomplete oxidation of juvenile $H_2S$ evolved by fumaroles.[1]

Among other volcanic sublimates containing sulphur we must mention: *realgar* ($As_2S_2$), sulphates of sodium, potassium, copper, lithium, etc. Of the gaseous volcanic sulphur compounds the commonest are hydrogen sulphide ($H_2S$) and sulphur dioxide ($SO_2$), but there is a suggestion that the latter is formed by the oxidation of vaporous sulphur subsequent to its evolution.

In igneous rocks there also occur a great variety of minerals containing sulphur. Among these are: *haüynite* ($3NaAlSiO_4.CaSO_4$), *nosean* ($3NaAlSiO_4,Na_2SO_4$), *pyrites* ($FeS_2$), *pyrrhotite* ($Fe_7S_8$—$Fe_{11}S_{12}$); the rarer *molybdenite* ($MoS_2$) found in granites, *bornite* ($Cu_3FeS_3$) in pegmatite veins, in which are also found *zinc blende* (ZnS), *galena* (PbS), *chalcopyrite* ($CuFeS_2$), etc.

The majority of the other sulphur compounds (sulphides and sulphosalts) belong to the minerals of veins, especially ore veins, and are genetically connected with magma.

[1] The investigations of Bekker showed that the complete oxidation of $H_2S$ to $H_2SO_4$ takes place with the evolution of nearly four times as much heat as oxidation with the formation of free sulphur: $H_2S+O \rightarrow S+H_2O$.

The average content of sulphur in igneous rocks is given as 0·05% by weight. In sedimentary rocks it is markedly lower, but in the hydrosphere reaches 0·09% by weight.

In the cycle of sulphur compounds in the zone of weathering the following important phases are to be noted: (1) oxidation, hydration and solution, of juvenile compounds; (2) the entrance of sulphur into the composition of living matter from solution or its direct separation from the latter as sulphates; (3) putrefaction and humification of organic residues; (4) the secondary oxidation of the products of putrefaction and exchange reactions of various kinds.

Oxidation and hydration embrace both varieties of native juvenile sulphur and sulphur compounds. As a result of these processes there are formed various vadose sulphates: some of these are the products of direct oxidation, *e.g.*:—

$$PbS+4O\rightarrow PbSO_4.$$

Others are formed by the action on other minerals of the sulphuric acid formed by the oxidation of sulphur or hydrogen sulphide, *e.g.*:—

$$H_2O+SO_3+MgSiO_3\rightarrow MgSO_4+H_2O+SiO_2.$$

The sulphates so formed have not a uniform stability: some of them pass easily into the dissolved state ($Na_2SO_4$, $K_2SO_4$), others less easily ($CaSO_4$), a third group give up their bases easily:—

$$FeSO_4+Na_2CO_3\rightarrow FeCO_3+Na_2SO_4.$$

At any rate, sulphates are dissolved to a greater or less extent in vadose solutions. Being a constant element of protein compounds and frequently found in the essential oils (mustard seed, garlic, radish), sulphur is actively removed from solution by all plants.[1] Its content in plant ash is not very high, and as a rule, in agricultural plants, at least, its content is less than that of phosphorus, but it often exceeds the calcium content. Taking into consideration the constant presence of sulphur in the composition of both plant and

[1] Sulphates are the main form in which sulphur is taken up by the higher plants. The other sulphur compounds may even have a harmful effect on the plant.

animal organisms, we may assume that the total amount of sulphur in living matter at the present moment reaches a value that is considerable, absolutely and relatively (compared with the total S in the earth's crust). For certain lower organisms, as we have seen, sulphur is an essential part of their substance.

The decomposition of organic matter is a source of *vadose sulphur compounds*, primarily of $H_2S$, which on microbiological oxidation gives *vadose free sulphur*. It is necessary to remember, however, that the sulphur of proteins and organic compounds is not the only source of vadose sulphur compounds and free sulphur, but also sulphates that undergo the microbiological process of desulphofication (p. 41).

These processes take place over wide areas of the submarine, and subsoil, salinization regions, the more since the desulphofication micro-organisms can develop in the presence of the minimum of organic matter. A characteristic by-product of desulphofication is vadose colloidal ferrous sulphide ($FeS.nH_2O$):—

$$3H_2S + Fe_2O_3 = S + 2FeS + 3H_2O.$$

The oxidation of free sulphur and sulphides—a microbiological process, as we know, again leads in the end to the formations of sulphates. At various points in the cycle some or other quantity of sulphur may leave the crust of weathering and pass into the deeper shells of the lithosphere in sedimentary rocks. It leaves in the form of sulphates, in organic compounds preserved in coal and oil, as sulphides such as that same hydrotroilite which may crystallize while still in the crust of weathering to form marcasite and secondary pyrites ($FeS_2$). The enrichment of its molecule in sulphur takes place, apparently, at the expense of adsorbed $H_2S$.

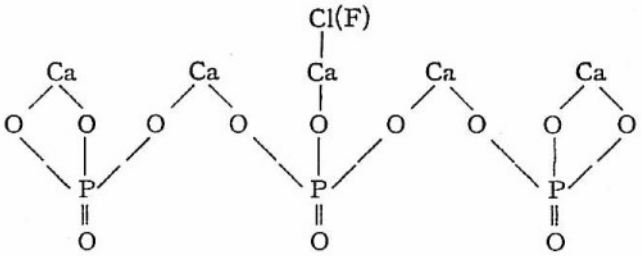
On the concentration of vadose solutions sulphates settle out with the salts of salt lake deposits and of soil and subsoil salinization. The main forms of these minerals have already been given (p. 140).

The related elements *selenium* and *tellurium* occur with the juvenile varieties of native sulphur. They are also found

in certain natural sulphides such as *aguilarite* $Ag_2(S,Se)$, *onofrite* Hg(S,Se), and form a small number of independent primary minerals with silver, lead, copper, mercury and gold: silver telluride AgTe, *petzite* $(Ag,Au)_2Te$, *berzelianite* $(Cu,Ag)_2Se$, *clausthalite* PbSe, *altaite* PbTe, *tiemannite* HgSe, *coloradoite* HgTe, *sylvanite* $AuAgTe_4$, etc. The weathering of these minerals leads to the formation of certain rare selenites and tellurites: *chalcomenite* $CaSeO_3.2H_2O$, *magnolite* $HgTeO_4$, *durdenite* $Fe_2(TeO_3)_3.4H_2O$. Nothing is known of the rôle of selenium in living matter.[1]

## 11. The Phosphorus Cycle. The Compounds of Arsenic

No less great a part than that of sulphur in the crust of weathering and especially in the biosphere is played by phosphorus, whose content in the earth's crust is about 0.1% (by weight). The typical juvenile forms of phosphorus are the varieties of *apatite: chlorapatite* $Ca_5(PO_4)_3Cl$, *fluorapatite* $Ca_5(PO_4)_3F$, and their isomorphous mixtures, which are the commonest. The molecular structure of these compounds may be represented thus:—




In small amount apatite occurs in almost all igneous rocks, but it is occasionally concentrated in pegmatite veins and even forms independent apatite veins. These concentrations are worked in certain areas—Canada, Norway, Spain, the Khibin Tundra of the U.S.S.R.

In addition to apatite, there are other phosphorus minerals in igneous rocks: *tripolite* $(Mn,Fe)_2FPO_4$, *ambly-*

[1] Cf. Selenium occurrence in certain soils of the U.S. *Tech. Bull.* 482, *U.S. Dept. Agric.*, 1935. K. T. Williams and H. G. Byers, *Ind. Eng. Chem.*, 1936, **28**, 912-914.

*gonite* $Li(Al,Fe)PO_4$, *monazite* $(Ce,La,Dy)PO_4$, *xenotime* $YPO_4$, etc., but all these minerals, and *pyromorphite* $Pb_5Cl(PO_4)_3$, are extremely rare, and the quantity of $P_2O_5$ combined in them is negligible. Thus, the main source of phosphorus in the crust of weathering is *apatite*, if we ignore the small amount of phosphorus which falls with cosmic dust. Apatite is a comparatively stable mineral, is only weathered with difficulty, but is soluble in acids.

Since the majority of vadose phosphorus minerals are of organogenic origin, it would appear that from the historical point of view the phosphorus cycle in the crust of weathering takes the following form: solution of juvenile compounds—absorption by organisms—the formation of vadose minerals—absorption again by organisms, and so on.

Apatite is insoluble in pure water, but in the process of secular weathering it finally dissolves in vadose solutions. This has been demonstrated by the direct experiments of R. Müller and C. L. Reese,[1] who showed that tricalcium phosphate is soluble in carbonated water. But it is obvious that vadose waters circulating in the crust of weathering at the present time obtain a considerable part of their phosphorus from much more readily soluble vadose phosphates. Phosphoric acid has been detected in small quantities or traces in river and spring waters; and occasionally individual cases that are rich in $P_2O_5$ have been found among the latter. For example, in France, Department of Seine and Oise, a spring contains $PO_4'''$ to the extent of over 20% of the total dissolved matter (1 litre contains 0·49 g., *i.e.* almost 0·05%).

Phosphorus is actively absorbed by organisms from solution and enters into the composition of animal and plant protein substances, phytine, lecithin, nucleine and other organic compounds of the plasma and nuclei of cells; it occurs in the bony tissue of vertebrate animals, and in the external skeletons of invertebrates (brachiopods, crustaceæ), as calcium phosphate.

As regards the higher plants, the acid exudations from their roots enables them to utilize the phosphorus of even difficultly soluble compounds. In this connexion there exist

[1] *Cf.* F W. Clarke, Data of Geochemistry, 5th Ed., pp. 523*ff*.

considerable differences not only among the phosphorus compounds, but also among the various kinds of cultivated plants as shown by Prianishnikov and Kossovich. Certain of these plants can utilize easily the phosphorus of some compounds from which others can obtain extremely little or nothing at all, and so, having no source of phosphate, perish. And although apatite is generally regarded as non-assimilable by agricultural plants, that does not mean that it cannot be utilized by others. There are reasons for believing that certain trees (pine, larch) may take up the phosphorus of apatite directly.

The amount of phosphorus absorbed by plants at the present time must be quite considerable, since in the ash of many cultivated plants it frequently exceeds the other elements, and the content of phosphoric acid may reach 50% (seed, meristematic cells). The ratio of phosphorus to the other ash elements in the composition of organisms is decidedly greater than that in natural solutions and soils, and in this way there is an enormous concentration of phosphorus in organisms.

As a result of this, organic residues frequently form the beginnings of vadose phosphorus minerals. It is just in this way that *vivianite* is formed during weathering under swamp conditions, in bones, or on the shells of animals. Other vadose phosphates of iron are often found in limonite beds, in the formation of which, as we have seen, organic matter (Fe-humus colloidal systems) takes part. To this type belong: *dufrenite* $Fe_2(OH)_3PO_4$, *strengite* $FePO_4.2H_2O$, *cacoxenite* $Fe_2(OH)_3PO_4.4H_2O$, *calcioferrite* $(Ca,Mg)_3(Fe,Al)_3(OH)_3.(PO_4)_4.8H_2O$, etc. Of the vadose aluminium phosphates formed in the same way the following are known: *wavellite* $Al(OH)_3(PO_4)_2.5H_2O$, *fischerite* $Al_2(OH)_3PO_4.2.5H_2O$, *callaite* $Al_2(OH)_3.PO_4.H_2O$, and other analogous compounds. The process which resulted in the formation of these minerals appears to have been the adsorption of $PO_4'''$ from solution by the positively charged hydrated oxides of iron and aluminium and their subsequent crystallization. This is the more probable in that phosphates as a rule, owing to hydrolysis and the great solubility of the

anion, give acid solutions,[1] which ought to contribute to the positive charge of the ferriallite adsorption complex.

A considerable source of phosphorus is provided by the deposits of excrements of birds and bats known as guano, which occur on the sea coasts of continents and islands and in caves. In these deposits are formed a number of vadose minerals consisting of neutral and acid calcium, magnesium, and ammonium phosphate: *monetite* $HCaPO_4$, *brushite* $HCaPO_4.2H_2O$, *martinite* $2H_2Ca_5(PO_4)_4.H_2O$, *collophanite* $Ca_3(PO_4)_2.H_2O$, *bobierrite* $Mg_3(PO_4)_2.8H_2O$, *newberyite* $HMgPO_4.3H_2O$, *hannayite* $Mg_3(PO_4)_2.2H_2NH_4PO_4.8H_2O$, *struvite* $NH_4MgPO_4.6H_2O$, *stercorite* $HNaNH_4PO_4.4H_2O$. All these minerals are more or less soluble: therefore water filtering through the guano beds becomes enriched in phosphoric acid and reacts with the underlying rocks, causing their phosphatization, *i.e.* the formation of the phosphates of the alkaline earths, aluminium, iron, etc. The phosphatization of a trachyte on an island in the North Pacific, and of an andesite on the coast of Martinique, have apparently resulted from this process. Other such cases are also known.[2]

Rivers carry phosphate to the sea, in which it becomes available to marine organisms. These take it up in lesser quantity than land organisms, as is shown by the phosphate content in their remains: fish bones, shells of invertebrates. If the shells of molluscs are largely composed of calcium carbonate, those of the brachiopods frequently have a very high phosphate content. Thus in the shells of *Lingula anotina* Gmelin, $Ca_3(PO_4)_2$ amounts to nearly 92%. There is also a considerable concentration of phosphorus in the remains of crustaceæ. In the outer skeleton of present-day crayfish the $P_2O_5$ content reaches 3% or more, but in the remains of Cambrian trilobites it attains 17%. Marked quantities of phosphorus are also gathered by annelids and marine plankton.

[1] F. W. Clarke, The Data of Geochemistry, p. 524. *Cf.* I. Antipov-karataiev and Nikolsky, The Nature of the Soil Adsorption Complex, Leningrad, 1933 (Russian).

[2] Clarke, *loc. cit.*, p. 529. A. D. Arkhangelsky has devoted special attention to this process of phosphate concentration, and states that many occurrences of phosphate of this type are missed during exploration. *Cf. Proc. Acad. Sci., U.S.S.R.*, 1930, A, No. 5.

This concentration of phosphorus by marine organisms on further alteration yields formations such as concretions, nodules, spheroids, etc., consisting mainly of calcium phosphate, and found in abundance both in the deep water red mud and in the shallow-water glauconitic deposits. In these phosphorites there is usually a certain amount of calcium carbonate present, with the result that when they are raised into land together with other marine sediments they usually become enriched with phosphoric acid at the expense of calcium carbonate, which is leached out. It might be mentioned that various phosphorites contain calcium phosphate of varying solubility and consequently of varying availability to plants.

Thus, the most widespread compounds of phosphorus in the crust of weathering are the phosphates of calcium, iron and aluminium with the first greatly predominating, giving both juvenile and vadose forms and being present as such in organisms (besides the already noted forms of phosphate in the bones of vertebrates and crustaceæ, germinating seeds separate free calcium phosphate which the plant organism conserves in its composition). In these forms phosphorus leaves the cycle of the crust of weathering for the deeper shells.

Of the other elements of the same group the most important in the crust of weathering is probably *arsenic*, whose primary compounds are analogous to those of sulphur. This analogy is retained in the vadose *arsenates*. There is no doubt that arsenic plays a certain part in living matter, since it is found in plants and marine organisms. In sea water arsenic is present to the extent of 0·01 to 0·08 mg. per litre. The power of arsenic, noted by physiologists and medical workers, to stimulate and increase the exchange of matter in the human organism shows that it is not altogether one of the elements that are indifferent in living organisms.

CHAPTER V

# FORMS OF THE CRUST OF WEATHERING AND THEIR DISTRIBUTION

## 1. Residual and Mobile Products of Weathering

Up to the present we have considered the processes leading to the alteration, in the crust of weathering, of the compounds of each element individually, but in nature these processes are obviously not isolated from one another. Occurring in all rock outcrops, they combine to give a complicated series of reactions whose interplay results in those accumulations of clastic materials known as products of weathering. These are extremely diverse both in the composition and state of their constituents. But the products of weathering are not retained entirely in this complex mixture, and, while the accumulation is taking place, undergo a certain amount of differentiation and regrouping, during which some are separated from others. This redistribution in space and time depends primarily on *the varying mobility of the different compounds* of which the products consist. The degree of mobility, *i.e.* ability to be transported, coincides to a great extent with the ease of *dispersion* of the compound, and it is evident that the most mobile are those which pass most easily into the state of highest dispersion, *i.e.* molecular solution in water,—that most powerful and universal means of transport and redeposition of material in the crust of weathering. Unceasingly, since the moment the lithosphere became covered with its mantle of water and air, the processes of weathering have carried out their work in the redistribution of the weathered material. Part of this is carried by ice and water away from the site of formation at different speeds depending on the degree of dispersion of the material, the magnitude of the transporting forces, and the nature of the path along which transportation takes place.

This material, transported as solid or solute, interacts with the rain water forming rivers and streams, and ought finally to reach the sea or other closed basin carried by the rivers dissecting the crust of weathering and by internal waters. But the distribution of these depressions is not invariable: if the bottoms of seas and oceans are raised into mountains with watersheds, then the sediments composing them, sometime products of weathering borne from the land; which have become transformed, not only undergo weathering, but, in addition, there begins a *new cycle of distribution* of these new products of weathering by some part or other of the new network of surface and underground waters which carry the products to the new depressions. We shall now consider the work of these cycles in their natural sequence, beginning with the first cycle, *i.e.* the weathering of primary rocks (igneous), in which the minerals *undergo weathering for the first time.*

First of all it should be noted that in the final analysis there is not one element occurring in rocks that is not carried in some form or other to the end-points of water transport. Leaving out of account the finest particles of comminuted primary minerals which may reach areas of water and be deposited in marine, lacustrine and river sediments, these substances, to a greater or less extent, pass into the dissolved state; we know that a complete and accurate analysis of sea water shows the presence of practically all the commoner elements of the lithosphere, even gold. Nevertheless, the quantitative compositions of the lithosphere, of river, and of sea water, in the same way as the quantitative compositions of primary rocks and aqueous sediments, are fundamentally different, and the quantitative composition graphically reflects the varying mobility of the products of weathering. From a study of the available data we may differentiate these compounds by their mobility.

In Table VI are given, in the first column, data for the average composition of igneous rocks;[1] in the second, the average composition of the *mineral* matter dissolved in

[1] A. Fersman, Geochemistry of Russia, 1922. Alkalis and alkaline earths recalculated as cations; sulphur as $SO_4''$.

rivers, whose catchment basins are mostly in areas of massive rocks and their products of weathering.[1]

TABLE VI

| | Average Composition of Igneous Rocks. | Average Composition of the Mineral Residue of River Waters. | Relative Mobility of elements and compounds. |
|---|---|---|---|
| $SiO_2$ | 59·09 | 12·80 | 0·20 |
| $Al_2O_3$ | 15·35 | 0·90 | 0·02 |
| $Fe_2O_3$ | 7·29 | 0·40 | 0·04 |
| Ca | 3·60 | 14·70 | 3·00 |
| Mg | 2·11 | 4·90 | 1·30 |
| Na | 2·97 | 9·50 | 2·40 |
| K | 2·57 | 4·40 | 1·25 |
| $Cl'$ | 0·05 | 6·75 | 100·00 |
| $SO_4''$ | 0·15 | 11·60 | 57·00 |
| $CO_3''$ | —— | 36·50 | —— |

We see that the quantitative composition of the dissolved mineral matter in river water is fundamentally different from that of the rocks which have provided the mineral matter. It is seen, too, that chlorine, which forms an insignificant part of the fresh primary rocks, is more than 6% of the mineral residue. This has happened, not because chlorine from other sources has been introduced into river water, but because its compounds in the rocks are dissolved out very much more rapidly than those of other elements. Let us suppose that within a certain definite period of time, some mass of rock of definite size gives up all its chlorine to river water. If the compounds of sulphur in this rock had the same mobility as those of chlorine, the amount of $SO_4''$ in river water would be three times as great as that of $Cl'$, as it is in the rock (0·15 : 0·05 = 3), *i.e.* it ought to make up 20·25% of the mineral residue. Actually, it only amounts to 11·6%; thus sulphur, expressed as $SO_4''$ ions, has only dissolved to

[1] Material taken from F. W. Clarke, The Data of Geochemistry, 1924, the average of 30 analyses.

the extent of 57% of its content in the rock during that period. Using this method for the other elements we obtain the figures given in the third column. It will be seen that these figures may be arranged in groups according to their order of magnitude. Rearranged in this way, they give a clear conception of the successive phases of the products of weathering, thus:—

| | | | |
|---|---|---|---|
| Phase I | $Cl'$ | ... ... | 100 per cent. |
| | $SO_4''$ | ... ... | 57 ,, |
| Phase II | $Ca''$ | ... ... | 3·00 ,, |
| | $Na'$ | ... ... | 2·40 ,, |
| | $Mg''$ | ... ... | 1·30 ,, |
| | $K'$ | ... ... | 1·25 ,, |
| Phase III | $SiO_2$ | ... ... | 0·20 ,, |
| Phase IV | $Fe_2O_3$ | ... ... | 0·04 ,, |
| | $Al_2O_3$ | ... ... | 0·02 ,, |

In the first phase the products of weathering are deprived of the compounds of chlorine and sulphur. It is evident that, together with these anions, cations must also be removed, but the greater portion of the latter remains, combined with other anions, mainly, of course, as silicates.

In the second phase, the primary products of weathering, already devoid of chlorine and sulphur compounds, begin to lose the alkali and alkaline earth bases. This phase is subdivided into two stages corresponding to the greater mobility of the lime-soda compounds in comparison with those of magnesia and potash (pp. 124 *et seq.*).

In the third phase, the bulk of the alkalis and alkaline earths have been removed and the silica of the alumino-silicates begins to move. And, finally, in the fourth phase, when the residual products of weathering consist almost exclusively of sesquioxides, these also undergo a certain amount of transference.

It should be mentioned that in the great majority of analyses of river water only the total sesquioxide content ($R_2O_3$) of the mineral residue is given, so that the relative mobilities of alumina and iron compounds are based on a few determinations only. The most we can say is that the compounds of iron and aluminium pass into solution in river

water and are borne away from the site of the accumulation of the products of weathering more slowly than silica, but whether the mobility of iron is twice that of aluminium still remains in doubt.

## 2. Distribution Cycles of the Products of Weathering. Phases in the Development of Orthoeluvium

As with every abstract scheme, the division of weathering into phases, such as given, obviously cannot be found displayed in nature in all its fullness. One reason, at least, is because there occurs nowhere the completely isolated weathering of single blocks of rocks. Nevertheless, if we introduce into our scheme certain additions, which are dictated by actual processes, it fits well, and from it we can elucidate fully the real relations in the crust of weathering.

First of all, it must be said that, for obvious reasons, weathering cannot possibly occur throughout the whole of an outcropping rock mass, individual blocks and fragments, for the outer surface of each piece will weather more rapidly than the interior. The products of weathering of primary rocks, therefore, will, in the majority of cases, contain not only *residual, i.e.* unremoved compounds of different phases, but also the primary minerals, and we can only refer any residual mass of weathering to the corresponding phase according to the predominance of one or other of these groups.

It is also extremely important to make a reservation regarding data for the content and the mobility of silica given in the table. It will be remembered that silica occurs in primary rocks in two main forms: free silica in the shape of quartz and the combined silica of silicates and aluminosilicates. The first is exceptionally stable, and there is no doubt that it possesses considerably lower mobility and solubility than do the alumina and iron compounds in the crust of weathering. It is therefore natural to introduce the silica of primary quartz into the fourth phase together with the sesquioxides. For this reason, in calculating the mobility of silica we took, not its total content in rocks, but only the amount of silica in silicates and aluminosilicates,

which was taken as 40%. This correction, however, does not affect the calculation to any extent and does not change the order of mobilities.

Finally, it is necessary to take into consideration the fact that the products of weathering receive material not only from the lithosphere, but also from the atmosphere, in that they become oxidized, carbonated and hydrated. In expressing iron and sulphur in combination with oxygen in the table, we have already taken oxidation into account to some extent. It is now necessary to add the formation of carbonates and the hydration of the products of weathering. Owing to their easy solubility the carbonates of the alkali metals ought to be washed out from the residual products in the same phase as chlorides and sulphates, but the alkaline earth carbonates, and especially the very common calcium carbonate, will be held in the second phase, at least in its early stages. Water of hydration, which ought to be the greater the longer weathering is prolonged or the more intensive it is, ought to accumulate to the greatest extent during phases III and IV of the residual material. And now, after these essential corrigenda, we may put the question—in how far does our scheme, to a considerable extent deductive, correspond to concrete, natural, formations and to what extent do they confirm it?

It will be necessary to look for pure forms, so to speak, of accumulations of residual products of weathering in those places in which there can be no possible influx of other products, and from which the residual products may, to a greater or less extent, be removed. In other words, such accumulations of residual products are typical forms of eluvium.

In studying the crust of weathering in areas of primary crystalline (or highly metamorphosed) rocks, we usually encounter deposits of large fragments, rubble, or coarse sand, consisting of particles of the disintegrated rock. The accumulation of this exclusively coarse material occurs when the energetic action of the forces of denudation, and especially of water, carries away not only the dissolved, but also all the fine material, leaving behind only the larger

fragments and blocks; of such origin is the residual crust of weathering in mountainous regions where ice as well as water is active, and to the same groups may be referred the coarse rubble on the bare desert-like mountains in the middle of continents from which the wind carries away all the fine material. In all these cases we must obviously not expect that the composition of the residual material will show a noticeable loss of chlorine and sulphur, for here new debris from the country rock will constantly be formed, and the chemical composition of the debris will hardly vary much from that of the fresh rock. This is now no longer the hypothetical, but the actual first phase of the residual products of weathering of primary (igneous) rocks. This we shall call coarse detrital *orthoeluvium*.[1]

But we encounter other cases in which the accumulated products of weathering are covered by a vegetation, which weakens the effect of mechanical denudation, and because of which only the soluble material is washed out. Thus, in the mountainous steppes of Northern Mongolia, Southern Transbaikal, and Armenia we frequently find masses of granites, gneisses, basalts and other igneous rocks whose flat summits and gentle slopes are covered with coarse detrital material, with a certain amount of fine earth in the interstices. If pits are opened to some depth in such weathered material where the debris is very coarse and close to the fresh rock, or to rock which is simply rotten along cleavage planes, we frequently observe small deposits of calcium carbonate. This carbonate, in the form of white films or thin crusts with small stalactitic outgrowths, covers the individual fragments (mostly the lower surfaces). The material for the formation of this salt is apparently the calcium of the fine earth and the $CO_2$ of the air circulating among the products of weathering. It is certain that some part of it is also formed by the mineralization of organic residues.

Where rock massifs with such a calcareous crust of weathering become dissected with the formation of closed, or

[1] This term is applied to the eluvium of primary (igneous) rocks in contrast to the *paraeluvium* of sedimentary rocks, and the *neoeluvium* of drifts. These will be discussed below.

almost closed basins, we frequently observe the permanent or periodic accumulation of saline water enriched with chlorides and sulphates in these basins. It is evident that in these examples we do not find the complete removal of chlorine and sulphur from the residual mass, if only because these elements, and especially sulphur, are taken up by organisms to some extent, but nevertheless there is an obvious washing out of their compounds.[1]

Thus, we have encountered in nature the *second phase* of the residual products of the weathering of primary rocks: we shall term it *calcareous orthoeluvium*. It coincides to a considerable extent with our first hypothetical phase, and is characterized by the washing out of chlorides and sulphates, and, at the same time, by the comparative stability of calcium compounds specially emphasized by the presence of its carbonate in the residuum.

The subsequent third phase is equally real, and consists of the *siallitic orthoeluvium* that we observe on the flat summits of the igneous rocks massifs of Middle Europe (Mittelgebirge), and Fennoscandia, on the mountainous taiga of Asia, North America, etc. There we may observe over wide areas rubbly residual products of weathering with a dense cover of grasses, or, frequently, mosses or forest litter. Nevertheless, in pits dug deep enough to reach the fresh country rock, we do not observe any deposits of calcium carbonate visible to the naked eye; nor is its presence indicated by effervescence with hydrochloric acid; but, under the microscope, minute crystals of calcite may be seen on slides made from rock fragments. When under local conditions rainfall is so high that $CaCO_3$ is not allowed to accumulate noticeably in the residual products, the second phase may not be expressed to any extent, and the orthoeluvium will consist predominantly of products of the third phase. A comparison of their composition with that of the fresh rock is given in Table VII, and shows fairly clearly the nature of the process. If we recalculate these results on an ignited basis (less water and humus) we shall be convinced that the

[1] N. Lebedev and I. Neustruev, Investig. Mongol and Tuvin Repub., 1930, pt. A, *Acad. Sci., U.S.S.R.*

weathered material has lost a large quantity of silica and much of its calcium and sodium compounds. This loss is reflected in the relative increase in the content of sesquioxides, whilst a considerable part of the ferrous iron has been converted into ferric. There is no decrease in the

TABLE VII

| | Fresh gneiss, St. Margen, Schwarzwald. | Weathered material. |
|---|---|---|
| $SiO_2$ ... ... ... ... | 68·55 | 51·78 |
| $Al_2O_3$ ... ... ... ... | 16·48 | 18·81 |
| $Fe_2O_3$ ... ... ... ... | 0·82 | 5·36 |
| FeO ... ... ... ... | 3·46 | 2·40 |
| MgO ... ... ... ... | 1·13 | 1·67 |
| CaO ... ... ... ... | 1·82 | 0·92 |
| $Na_2O$ ... ... ... ... | 3·43 | 0·88 |
| $K_2O$ ... ... ... ... | 1·47 | 1·72 |
| Organic matter + $H_2O$ | 2·05 | 15·70 |

TABLE VIII

| | Fresh granite porphyry. | Weathered material. |
|---|---|---|
| $SiO_2$ ... ... ... ... | 70·25 | 61·45 |
| $Al_2O_3$ ... ... ... ... | 14·01 | 17·07 |
| $Fe_2O_3$ ... ... ... ... | 1·12 | 4·91 |
| FeO ... ... ... ... | 1·59 | 1·59 |
| MgO ... ... ... ... | 0·94 | 2.10 |
| CaO ... ... ... ... | 0·86 | 0·28 |
| $Na_2O$ ... ... ... ... | 2·63 | 0·95 |
| $K_2O$ ... ... ... ... | 5·97 | 1·70 |
| Organic matter + $H_2O$ | 1·35 | 9.12 |

amounts of potassium and magnesium; their percentage content has actually increased owing, of course, to the great decrease in silica and other compounds. The comparison

of the results for fresh gneissose granite-porphyry and its residual products of weathering from Graubünden (Alps), given in Table VIII,[1] leads to the same conclusions. The one difference is that in this case the compounds of potash are markedly washed out of the residual products, and only the magnesium compounds continue to show a high stability.

In these cases it is seen that real examples of *siallitic orthoeluvium* coincide very closely with our second hypothetical phase and its stages of development.

In this phase of siallitic orthoeluvium the aluminosilicates of the first group ought gradually to pass into *residual aluminosilicic acids, i.e.* acids of the kaolin type. But since other groups do not retain the union between alumina and silica on decomposition, and since dispersed and dissolved silica and alumina have many opportunities of precipitating from solution, it is possible that allophans (pp. 94 *et seq.*) may be formed to some extent, although under the conditions obtaining in the eluvium they will be unstable and easily carried away in solution.[2]

The examples of orthoeluvium just given show an accumulation of sesquioxides at the expense of the leaching out of the alkalis, alkaline earths and silica. But other cases are known in which this process has entered another phase, which is marked by the almost negligible amounts of the alkalis and alkaline earths, so negligible that, in practice, they may be considered absent. These cases belong to the so-called *lateritic* crust of weathering occurring in many parts of moist tropical countries at the present time. In the subjoined Table there is provided a comparison of the composition of some crystalline rocks with that of the lateritic crust formed from them (Table IX). It hardly requires any

[1] These data are taken from the article by Prof. H. Harrassowitz, "Boden der feuchtwarmen gemassigten Regionen," in Blanck's *Handbuch der Bodenlehre*, Bd. III, Berlin, 1930. Harrassowitz cites these results as examples of a special type of "yellow-soil" weathering peculiar to a warm, moist, climate in temperate latitudes. To what extent we may speak of the dependence of weathering on climatic conditions will be discussed below.

[2] Nevertheless, the accumulation of pure kaolin, as a result of weathering, is only likely under extremely favourable conditions, when not only the alkalis and alkaline earths and the excess of silica, but iron also, is washed out.

recalculation of the figures to see that the products of weathering have lost an enormous quantity of silica, have been hydrated, and lost almost all of their alkali and alkaline earth bases. Careful consideration of the relations between aluminium and iron shows that the relative accumulation of iron in the first case (gneiss from Colombo) exceeds the relative accumulation of aluminium, and while in the fresh gneiss the amount of iron present as ferric oxide is less than half that of alumina, it rises to four-fifths of the alumina in the weathered material. It is necessary to assume that a certain part of the alumina (apparently in the form of allophans) also quits the products of weathering. In the second case (diabase from Guinea) the ratio between iron and aluminium in the products of weathering is approximately the same as in the fresh rock.

TABLE IX

LATERITIC WEATHERING

| | Fresh Gneiss from Colombo. | Weathered material from the gneiss. | Fresh diabase from Guinea. | Weathered material from the diabase. |
|---|---|---|---|---|
| $SiO_2$ ... ... ... | 64·42 | 33·87 | 51·27 | 5·83 |
| $Al_2O_3$ ... ... ... | 17·25 | 26·57 | 12·36 | 37·03 |
| $Fe_2O_3$ ... ... ... | 4·21 | 19·69 | 3·29 | 31·73 |
| FeO ... ... ... | 3·95 | 0·65 | 6·16 | —— |
| MgO ... ... ... | 0·49 | —— | 13·26 | 0·06 |
| CaO ... ... ... | 2·10 | —— | 10·66 | 0·19 |
| $Na_2O$ ... ... ... | 2·42 | tr. | 1·60 | —— |
| $K_2O$ ... ... ... | 2·99 | tr. | 0·41 | —— |
| Org. matter + $H_2O$ | 0·94 | 17·82 | 0·40 | 23·02 |

These concrete examples indicate that there are in nature real residual products of weathering corresponding to our third hypothetical phase and partly to the fourth. We refer these cases to the fourth phase of residual products of weathering of primary rocks, and shall call this phase the phase of *allitic orthoeluvium*.

But the presence of the forms of accumulation of products of weathering just considered are still not proof that they are essentially phases of one process, as follows from the scheme we have constructed. Still more doubts may arise because many contemporary workers regard these formations as the results of *specific, dissimilar* types of weathering, each characteristic of *distinct climatic conditions*. From this point of view there exists between climate and the products of weathering a *definite equilibrium* and a *constant relationship*. We shall return later to the criticism of these views and the basis for the study of phases of weathering, but at present we must consider still another, so far deductive, scheme.

### 3. Forms of the Accumulative Crust of Weathering. Distribution of Residual and Accumulative Products of Weathering in Relation to Geomorphological Conditions

Up to the present we have discussed *residual* products of weathering only, leaving out altogether the fate of those that are carried away from the eluvial accumulations to be deposited elsewhere on the earth's surface. Let us accept as true the phase theory of the residual products of weathering, and imagine that the watershed of some igneous massif (*Fig.* 4, p. 174) has reached the last phase of weathering and is covered to some depth with *allitic orthoeluvium*. During the weathering of the rock some of the products have been carried away from the higher points either to form the covering of colluvium on the slopes, or still further afield to be deposited in the nearest basin—let us assume, under marine conditions. It is evident that the loose material which forms the colluvium and the littoral deposits may consist of the most diverse constituents from fragments of fresh minerals and rocks to the fine particles of the allitic crust of weathering. But if we take into consideration the order of mobilities of the products of weathering (p. 163) we must assume also that the compounds of chlorine and sulphur, sometime part of that mass of rock which is now changed to allitic orthoeluvium, will have been carried away earlier and further than

the other products. It is natural to expect that they will be carried to the sea, but there is a large body of evidence to show that a certain portion does not reach the sea but appears in the deposits of the seashore and neighbouring territory. Such accumulations of chlorides and sulphates become understandable if we analyse the mechanism of their transport and deposition. Returning to the colluvium of the primary rocks it must be assumed that the solutions bearing the soluble products of weathering flow both in the form of surface streams cutting into the mass of deposits and as periodic or permanent streams of ground and subterranean waters (most probably at the junction of the massive rock and the loose deposit) percolating through the deposits. But these ground waters occur not only in the form of gravitational streams, but may rise vertically as capillary or pellicular water, and on evaporation salinize the deposit to a considerable depth. It is evident that this salinization will take place the more rapidly, the nearer the level of the saline ground water is to the surface and the less rainwater there is percolating from above.

We have already given examples of the formation of chloride-sulphate lakes in depressions among the massive igneous rocks of Northern Mongolia (p. 167). It is only necessary to add that the deposits surrounding these lakes are fairly saline. But such formations are, of course, known in places other than Gobi and Northern Mongolia. Closed basins in drifts rich in salts, and salt lakes whose water-catchment area contains salt deposits, are characteristic of the majority of deserts and arid steppes.

It can hardly be doubted that these formations demonstrate, in miniature, phenomena on a much greater scale,—the accumulation of salts in sea and ocean basins, and the formation of littoral forms of chloride-sulphate-accumulations.

But it must not be thought that this salinization occurs solely in river deltas and in low-lying flat littoral plains of the Precaspian type, where it frequently appears in the form of surface solonchaks, and where its source may be sea water itself. Surface solonchaks are only an exceptional case of the salinization of the subsoil (*grund*) in which the salts reach

the surface. There is, however, in Southern Russia a wide area stretching for hundreds of kilometres that obviously contains chlorides and sulphates in those horizons lying above the ground water table. This salinization apparently is due to the salts collected by solutions feeding the ground waters from extensive salt catchment areas. It must not be assumed, however, that these forms of chloride-sulphate salinization by waters that do not reach marine or lacustrine basins are characteristic exclusively of deserts, or in general of countries with a clearly expressed continental climate. It cannot be denied, of course, that increased evaporation raising the concentration of salts in soil and ground waters ought to facilitate salinization, but it likewise cannot be denied that very definitely salinized deposits can be found in regions that are by no means dry. Thus, there are wide areas of salinization in the low foothills on the western coast of Formosa,[1] in the deltas of the Indus and the Ganges, and on the Bengal shores of Hindustan.[2] The present author has shown the presence of chlorides and sulphates on the shores of Lake Paleostom and the mouth of the Rion (Georgia). All these are regions in which the annual rainfall amounts to thousands of millimetres. Of a more continental type, yet far from being desert, are the saline soils of depressions with limited outlets in Central Norway and in the Yakutsk province, and of the littoral deposits at the mouth of the Yenisei.

And so a great number of concrete examples justifies us in speaking of a *chloride-sulphate form,* this time not of the residual, but of the *accumulative* crust of weathering. This form appears in the saline sediments of closed basins, valleys with only slight fall, the lower parts of slopes, *i.e.* the alluvial, colluvial and fanglomerate deposits, but, of course, never in eluvium.[3] We shall leave a place for this form in our scheme (*Fig.* 4) and turn now to further consideration of the formation of accumulative forms of the crust of weather-

[1] See soil map of Formosa by Professor Seki included in the article, "Soils of Japan," by O. N. Michailovskaya. Contributions to the knowledge of the soils of Asia, Part 1, Leningrad, 1930.
[2] See the article by Z. J. Shokalskaya, *Ibid.*, Part 2, 1932.
[3] Mention will be made later of cases of the salinization of soils on watershed plateaux.

ing. We saw above that not only many primary compounds of the alkalis and alkaline earths, but also such products of weathering as calcium carbonate, are much more stable and less mobile than the compounds of chlorine and sulphur. It is thus evident that the area of drift in which capillary and pellicular water will precipitate and deposit calcium carbonate will be greater than the area of chloride-sulphate accumulations, and will even include the latter. Suppose this is the area represented in *Fig.* 4. To what extent, it might

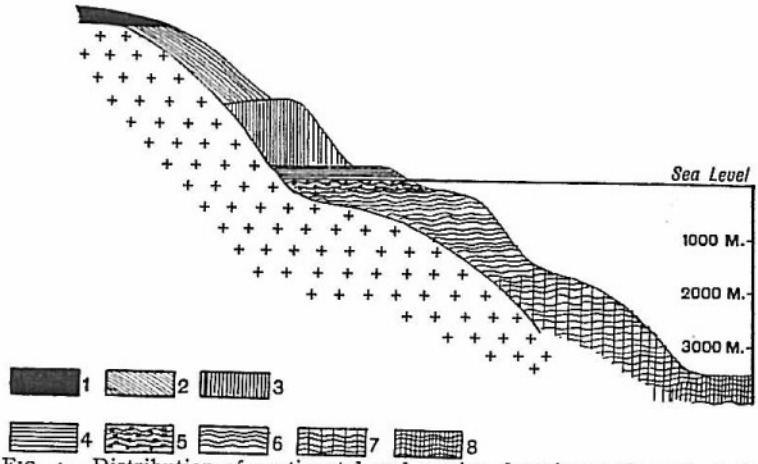



FIG. 4.—Distribution of continental and marine deposits at the end of the first cycle of weathering. 1. Allitic eluvium; 2. Siallitic (allophanic) accumulations; 3. carbonate accumulations; 4. chloride-sulphate accumulations; 5. coastal deposits; 6. terrigenic muds; 7. pelagic muds; 8. deep-water red clay. The massif of igneous rock is indicated by crosses.

be asked, do facts support the hypothetical formation and position of such a calcareous accumulative crust of weathering?

Among continental deposits, scientists have devoted and continue to devote great attention to the loess which covers such extensive areas in Eurasia and America, and about whose origin the most divergent views have been advanced.

One of the protagonists of the æolian theory of loess formation, Prof. V. I. Krokos, of Odessa, has recently published a thorough investigation of the Ukrainian loess in which he gives innumerable analyses covering the whole

depth at certain points.[1] It must be said that this excellent work in no way confirms the æolian hypothesis. Thus, from the analyses it can be seen that the ratio Ca : Al in the Ukrainian loess approximates to unity; but among primary rocks such ratios are only encountered in certain comparatively rare basic igneous rocks. It is therefore evident that a considerable part of the lime, and that in the form most characteristic of loess—$CaCO_3$, *was formed not in the loess by weathering,* but was introduced from outside either during, or after, the deposition of the loess.

If we consider certain general properties of loess: the occurrence of small round pores, and its power to form vertical escarpments, it is not difficult to imagine how this carbonate was deposited. Indeed, experiments show that during the capillary rise of bicarbonates, *e.g.* $NaHCO_3$, in soil, intensive separation of $CO_2$ takes place and the salt changes into the normal carbonate.[2] The same thing will happen during the capillary rise of calcium carbonate. It is natural also that the calcium carbonate precipitated in the *ascending* capillaries will cement the loess in such a way that blocks of it will break off much more easily along vertical than along horizontal or inclined planes. We can thus assume that the calcareous south Russian loess is a region of concentration of that lime (and partly magnesia) which was lost in solution at some time by the morainic drifts adjoining the loess on the north, and now to a considerable extent depleted of their alkali and alkaline earth bases, and in particular of calcium. Analogous relations may be observed in over more limited areas in Northern Mongolia, where the leached crust of weathering covering the summits and upper slopes of the Kentei and Khangai massifs passes at lower levels into a mantle of calcareous loess, and the latter, in the region of river and lacustrine alluvium, into chloride-sulphate accumulations (valleys of the Khara, Tola, and Lake Ikhe-Tukhumnoor).

[1] *Journal Scientific Investigations,* Odessa, 1926, **2**, No. 4. In the tables of analyses the CaO shown does not include that of $CaCO_3$, which is given separately.

[2] See B. B. Polynov and B. Philosofov, *Ann. Sci. Melioration Inst.* (Leningrad), 1930, pt. 21.

Above the calcareous accumulations in our scheme there ought to be an area of drift from which chlorides, sulphates and calcium carbonate will be leached out, and in which migrating silica may be deposited; but this will take place slowly. This silica, together with the residual alumino-silicic acids of the drift and a certain amount of sesquioxides from the allitic eluvium, confers the predominantly allophanic character on such a siallitic carbonate-free drift.

Concrete examples of siallitic (loamy and clayey) drifts, leached, and depleted to a considerable extent of their bases and $CaCO_3$, are sufficiently numerous and well known in the form of the *colluvium* covering the slopes of primary rock massifs in Europe, Fennoscandia, the mountain taiga of Eastern Asia, and Northern Mongolia, but there exist examples showing the relationship of these drifts to allitic orthoeluvium, which just as definitely fit into our scheme. Such a case is found in Hindustan, where typical laterites, according to direct observation, are confined solely to the watersheds of high plateaux,[1] while at lower levels (terraces, valleys), if we disregard the secondary deposits from above, they are not developed, giving place to the usual siallitic (clayey) drifts. But it is hardly likely that these secondary deposits will retain their allitic nature. Since they obtain solutions from above, including silica, their composition must be fundamentally altered. So we find support for the existence of the third phase of the accumulative crust of weathering—the siallitic carbonate-free. With considerable probability we may assume that the accumulative siallitic crust of weathering is distinguished from the siallitic orthoeluvium (residual crust) by the predominance of aluminosilicic complexes of the allophane type (p. 94), while in orthoeluvium there ought to predominate the residual alumino-silicic acids (of the kaolin type).

Thus, primary massive-crystalline rocks give the following principal forms of the crust of weathering:—

I. *Residual: (a) coarse detrital, (b) calcareous, (c) siallitic, (d) allitic, orthoeluvium.*

[1] *Cf.* Z. J. Shokalskaya, The Soils of India; also, the paper on the soils of Adzharia in *Trans. Dokuchaiev Soil Inst.*, 1933, **8**, pt. 4.

II. *Accumulative*: (*a*) *chloride-sulphate* (*predominantly alluvial*), (*b*) *calcareous* (*predominantly colluvial and proluvial*), and (*c*) *siallitic drifts*.

All these forms are, in our opinion, genetically related, and this relationship is shown outwardly in the dependence of their distribution on geomorphological conditions. This last may be formulated in the following three theses :—

I. *The calcareous orthoeluvium of watersheds is accompanied on the lower levels by an accumulative chloride-sulphate crust of weathering in the form of a drift* (*enriched with chlorides and sulphates*). *The salt catchment region for chlorides and sulphates is the whole thickness of the residual crust of weathering on the watershed* (*Gobi type*).

II. *The siallitic orthoeluvium of watersheds is accompanied on the lower terraces by calcareous accumulative, and, still lower, by chloride-sulphate crusts of weathering. In this case the whole thickness of orthoeluvium serves as the source of carbonates for the calcareous accumulation, whilst the chloride-sulphate crust receives its material from the orthoeluvium and the calcareous accumulation* (*Northern Mongolian type*).

III. *Allitic orthoeluvium of watersheds is accompanied by the distribution over lower levels of the following in the order given: siallitic, calcareous, and, at the lowest level, the chloride-sulphate crusts of weathering* (*Congo and Zambesi basin type*).

### 4. The Influence of Climatic Conditions on the Distribution of the Products of Weathering

The regularities that we have just deduced, although supported by individual cases, cannot by any means be regarded as universal laws governing the distribution of the products of weathering to which all cases would adhere. This is so, first of all, because the theses advanced are functions of one variable only,—the dependence on geomorphological conditions. The actual contemporary distribution of the products of weathering, as well as the composition of the products themselves, is much more complex and is dependent

to some extent on both climatic and historico-geological conditions. Let us consider, first of all, the rôle of climate in the formation of allitic orthoeluvium.

Laboratory experiments on the action of carbonated water on finely ground crystalline rocks and minerals show that, with a ratio of water to rock of 25 : 1 by weight, about 0·005% of the silica of silicates and aluminosilicates is removed. Recalculating, we find that, under conditions similar to those of the experiment, in a country with an annual rainfall of 1,500 mm., it would take about 500 years for the complete allitization of a 1 cm. layer of rock and 50,000 years for a 1 metre layer.[1] But since such favourable conditions never occur in nature, and rain water has to deal with massive compact rocks and not with finely comminuted powder, and since the great mass of the water (especially at high altitudes) does not manage to soak in, but runs off in streams, it is evident that these figures should be much increased, even for countries with 2,000 to 3,000 mm. annual rainfall. We thus, *a priori,* must conclude that the process of allitization, even under climatic conditions (moist tropical) facilitating intensive weathering, requires for the attainment of more or less definite results a very considerable time, measurable only on the geological scale.

This time our conclusion is confirmed by facts. It is well known that real examples of the formation of allitic products of weathering are confined, predominantly, to regions with a moist tropical climate which, *at the same time,* are the regions of the most ancient land (India, the Congo Basin in Africa, and the Amazon Basin of South America, are all referred by Suess to the ancient Gondwana land). But within that region the allitic crust does not form an unbroken cover. It is not observed either on the accumulations on the lower terraces and valleys, or on young (post-tertiary) igneous rocks. In this connexion the observations of H. Erhart in Madagascar are of special interest. There, on post-tertiary basalts with a well-developed crust of weathering, laterite is not formed, although it covers

[1] In this calculation we assume that one-third of the precipitation is lost by evaporation and that the total silica in the rock amounts to 40%.

the older basalts.[1] Harrassowitz, who has devoted a thorough investigation to laterites, could not find any clear indication of a lateritic crust of weathering on sedimentary, and observed it only on the more ancient igneous and strongly metamorphosed rocks.[2]

We thus come to the conclusion that the formation of the allitic crust of weathering is confined to the regions of moist tropical climate, not because this process is exclusive to that climate, but because at the present geological epoch the process of allitization has reached its greatest development in countries of the most intensive weathering, *i.e.* of moist tropical climate.

TABLE X

| | Fresh Tyrma granite. | Weathered granite. | Fresh S. Osetian argillite. | Weathered argillite. |
|---|---|---|---|---|
| $SiO_2$ | 74·90 | 67·83 | 78·44 | 69·94 |
| $Al_2O_3$ | 13·30 | 16·35 | 12·07 | 14·46 |
| $Fe_2O_3$ | 3·07 | 8·82 | 3·30 | 7·10 |
| MgO | 0·35 | 1·32 | 0·90 | 1·47 |
| CaO | 0·32 | 0·88 | 0·70 | 0·65 |
| $Na_2O$ | 4·08 | 1·87 | —— | —— |
| $K_2O$ | 3·49 | 2·23 | —— | —— |

If the above reasoning be correct, then it is logically possible for allitic products of weathering to be formed under other conditions. And we have at our disposal a certain number of facts which afford, if not direct, at least indirect, confirmation of this possibility. In Table X are given the results of the analysis of fresh granite from the basin of the river Tyrma (Amur province) and the weathered material,[3] and the composition of fresh argillite from the sub-alpine region of Southern Osetia and the products of weathering of that

[1] H. Erhart, Sur la nature et l'origine des sols de Madagascar, *Compt. rendus*, 1929, **188**, 1561.

[2] Harrassowitz, Laterit, Berlin, 1926. *Cf.* J. B. Harrison, The Katamorphism of Igneous Rocks.

[3] B. Polynov, Soils and Geography of the Tyrma Taiga, *Trans. Soil-Bot. Exped. Colon. Bur.*, 1909, Pt. 5, St. Petersburg, 1911.

argillite.[1] All values have been recalculated on a water-free basis.

If we compare these results with those given on page 168 (gneiss from Schwarzwald and granite-porphyry from Graubünden) as examples of the formation of siallitic orthoeluvium, we see an almost complete similarity in the relationships of the products of weathering to the original rock. It is broken only by the figure for CaO in the weathered material from the Tyrma granite, which apparently shows an accumulation of calcium. But this becomes clear if we remember that the products of weathering were in this case collected together with organic matter. This calcium had apparently been taken up by plants and retained in the humus. In any case the loss of silica and the gain of sesquioxides during weathering is just as clear as in the analyses of gneiss and granite-porphyry given by Harrassowitz. But it is necessary to note that Harrassowitz regarded these results as indicating a specific yellow soil (zheltozem) process of weathering characteristic of countries with a moist warm climate in temperate latitudes, and considered this yellow-soil process as a transition to the allitic, characteristic of moist tropical climate.

The Tyrma taiga is a region of everfrozen, where snow lies in the ravines all the year round, and like the subalpine zone of Southern Osetia cannot be considered as belonging to a warm region, so that it would be more correct to regard the data presented, both Harrassowitz's and our own, as demonstrating the formation of siallitic orthoeluvium,—a process no doubt transitional to the allitic, but by no means specific to any one climate, and at the present time occurring in countries with very different climates. This might be due either to the difference in time during which the process has been acting, or to the fact that under different climates the intensity of leaching may appear to be more or less the same. Indeed, as temperature falls so does evaporation, and therefore the effects of solution by surface and groundwater movements may be as great as in regions with a much higher temperature and annual rainfall.

[1] Investigation by O. N. Mikailovskaya, 1930; manuscript.

## 5. The Relation between the Solution and Deposition of Mobile Compounds in the Accumulative Forms of the Crust of Weathering

Turning to the calcareous crust of weathering, we see that its present distribution is likewise not confined to any definite climate. It is well known that, although calcareous loess is widespread in countries of dry and comparatively warm steppe climate, it, or its analogues, are not absent from the moister taiga regions, as is shown by the loess of the Dvina basin and carbonate accumulations in the tundra. Somewhat different is the case of the residual calcareous crust of weathering. Although known cases of its occurrence are confined to various, yet continental, climates, there are other facts which show that under certain climatic conditions it is hardly developed at all. In the taiga zone the weathering of primary rocks and the accumulation of the residual products are observed over extensive areas. But as has already been mentioned, the intermediate (calcareous) products are not present to any great extent in spite of the abundance of primary rock fragments and the accumulation of siallitic products. Nevertheless, since microscopical investigations show that carbonates are present,[1] we must conclude that with definite relations between the amount of rain and the calcium carbonate formed by weathering, the carbonate may not accumulate to a noticeable extent, and the general character of the products of weathering at once becomes *siallitic*. In these cases the phase of calcareous orthoeluvium in its typical form is omitted, but *the formation of $CaCO_3$ as a necessary element of the general process of weathering nevertheless remains.*

In those cases in which $CaCO_3$ is not only formed *in situ* but is introduced from outside, we may observe its accumulation at the present day even under conditions of a definitely moist climate; such, for example, as the carbonate alluvium of the lower reaches of the Ganges, the delta of the Rion (Georgia) and the lower littoral terrace of Southern Abkhasia. These are all in countries in which the annual rain-

[1] *Cf.* B. B. Polynov, Don Sands, their soils and land forms, *Trans. Dokuchaiev Soil Inst.*, 1927, vol. 2.

fall amounts to some thousands of millimetres, and in which the residual crust of weathering is of siallitic or even almost siallitic-allitic character. But it can be conceived that under a definite combination of conditions (composition of country rock, climate and relief) calcium carbonate will not be held in the drifts, but together with the chlorides and sulphates will be carried away to marine basins. In sea water it is widely utilized by organisms, and in general falls out of solution in some form or other. The sulphates and chlorides of sea water may cause the salinization of previously leached drifts of the lower beaches or river deltas where the sea water shades into the ground water and is raised by capillary action to give rise to a singular form of the chloride-sulphate crust of weathering. In this case a break occurs in our geomorphological sequence of the accumulative forms of the crust of weathering, and the siallitic accumulative crust on seashores passes directly into the chloride-sulphate, omitting the calcareous form (Holland). Nevertheless, in these cases the chloride-sulphate crust is not of continental salinization, but of marine or lacustrine origin, *i.e.* it is caused, *not by those solutions that have not yet reached a water reservoir, but by the solutions of the reservoir itself.*

According to certain workers the salinization of drifts, and especially the drifts of seashores, is explained by the introduction by rain water of salts dispersed in the air. The presence of chlorides and sulphates in rain is a fact confirmed by numerous analyses. These salts get into the air by the mechanical dispersion of sea water during storms, are carried away by wind and returned in rain to the land. In order to evaluate the importance of this phenomenon more accurately it is necessary to determine quantitatively the part of each of these salts in the process of salinization of littoral drifts.

Taking for the Black Sea—Sea of Azov coast, an annual precipitation of chlorine in rainwater of 13·12 kg. per hectare (Mariopol),[1] and expressing this value in terms of the whole

[1] P. S. Kossowitz, The Sulphur and Chlorine Cycles in the Earth, *Com. Bureau Agric. and Soil Sci.*, 1913, XII, p. 27 (Petersburg).

area of the Don Basin (400,000 sq. km.), we find that the total chlorine distributed over the area amounts to about $525.10^6$ kg. per annum. During the same time the Don discharges into the Sea of Azov over $1{,}500.10^6$ kg. chlorine.[1] It is thus obvious that the amount of chloride introduced into the soils by rain cannot explain the enormous amounts of chloride which are not yet washed out of the Don basin, occupy extensive areas of the Preazov steppes, and are expressed in the abundance of surface solonchaks occurring in the valleys of the lower Don, its branch Aksai, and its tributaries—Sal, Manych, Tuzlov, and other small streams and ravines.

So without denying the fact that salts may be carried by rain, it cannot be accepted as a full explanation of the accumulation of salts in soils and drifts.

We have already mentioned that chloride-sulphate accumulations may occur under various climatic conditions, and the examples given show fairly conclusively that in this case climate is important since it conditions the rate of solution, leaching and secondary separation of the salts.

We thus arrive at the general conclusion that climate, *i.e.* the hydrothermal conditions of weathering, has a substantial influence on the intensity of that process *without altering in the least its general direction;* and if at the present time we find that the calcareous orthoeluvium and accumulations are confined to dry steppe climate, and allitic orthoeluvium to a moist tropical climate, this is so, not because each climate has its own independent type of weathering, but because the processes of weathering at the present moment have attained different stages, viz., those that we now observe. This circumstance explains why the climatic factor appears to dislocate our scheme for the distribution of the products of weathering which was built up solely on a geomorphological basis (p. 171).

### 6. The Distribution of Marine Deposits

The actual distribution of the products of weathering that we observe on any land area at the present time frequently

[1] P. N. Chirvinsky, *N. Caucasian Amelioration Bull.*, 1919, No. 1-2 (Novocherkassk).

diverges from our scheme, not only under the influence of climate, but also, as already mentioned, on account of historico-geological conditions.

In order to elucidate the nature and form of these divergences we must first of all follow the movements of the mobile products of weathering right up to the moment of upheaval of sedimentary rocks above sea level and the beginning of a "secondary cycle" of weathering (p. 161).

The vast hollows in the earth's surface occupied by oceans and seas receive, not only compounds dissolved in water and carried by surface and ground water, but also a colossal amount of coarse and fine detrital material. This is borne by large rivers in the form of fine muddy suspensions of the products of weathering, while mountain streams that flow directly into the sea carry silt, sand, and much coarser detrital material. These are also continually supplied by the active work of waves breaking on the shore, disintegrating and comminuting coastal escarpments even when those consist of hard compact rocks. The products of this so-called *abrasive* action of waves, depending on their size, may be either left on the coastal *abrasion platform* or be carried out to sea by backwash or coastal currents.

The detrital material falling into the sea is sooner or later deposited on the bottom, but during that deposition, and subsequently, there occurs a complex interaction with the sea-water, the salts dissolved in it, and the organisms peopling it. The difficulty of observing and studying these processes is reflected in the slow growth of our knowledge, and conceptions of their diverse interrelationships have begun to take definite form only in comparatively recent times. Much light was thrown on this, still somewhat obscure, domain by the famous *Challenger* expedition of 1873-76. Of the numerous publications that resulted from the many years' study of the abundant material collected by the expedition there is for us a special interest in the work of the expedition's geologist, Sir John Murray.[1] In this work sea deposits received that natural classification which is based directly on their origin and is in agreement with

[1] Sir John Murray and A. F. Renard, Deep Sea Deposits (London, 1891).

their distribution. But before setting out this classification and the characteristics of marine deposits it is necessary to dwell for a moment on the processes that occur in the material brought into the hydrosphere.

The unusually constant composition of the mineral residue of sea water, as has been repeatedly mentioned, differs fundamentally from that of the river water flowing into it. This change in the composition of the dissolved compounds is reflected most clearly in the contents of chlorine, sodium, calcium, carbon-dioxide and silica, and the reasons for this have been discussed. We have already seen that the multitudes of marine organisms absorb calcium and silica for the construction of their shells and skeletons, and this process is so extensive that the content of silica in the mineral residue of rivers, which on the average is about 12%, and in many individual cases (tropical rivers) reaches 50% and more, decreases in the waters of the ocean to a few hundredths of one per cent.[1] The calcium content falls from an average of about 15%, and in individual rivers 25%, to 1·2% in the residue of ocean water. The same happens to carbon dioxide (from 34·5% to 0·2%). Inversely, the increase of chlorine from 7% to 55% in the residue of sea water is due, obviously, to the absorption of the other elements. It is an indication also of the lesser utilization of chlorine by organisms. The content of sodium is also considerably increased (from 9·5% to 30·5%) in the sea, as compared with rivers, but nevertheless this increase is less than that of chlorine. It is possible that sodium is absorbed to a greater extent than chlorine.

But in addition there are other ways in which sodium and other cations are absorbed from sea water, and these will be discussed later. It should be remarked here that if all the chlorine carried by river water were combined with sodium, in the residue from sea water it must be partially combined with other cations (*e.g.* magnesium).

The content of potash is clearly decreased (to 1·10%), but it is strongly absorbed by organisms. The absorption of

[1] Silica, however, is not only absorbed by organisms, but is also precipitated in gel form (*v. infra*).

magnesium and sulphur is reflected only slightly in the decrease in their relative contents ($SO_4''$ 7·6%, $Mg^{\cdot\cdot}$ 3·6%). Nevertheless, in comparison with sodium, whose amount has increased, this absorption must be great. Having at our disposal insufficient analyses containing results for other less common elements, we cannot judge to what extent they are absorbed from sea water, but individual examples have already been given (*vide* iodine, phosphorus).

It is necessary to note that for colloidally dissolved compounds, among which there may be silica, sesquioxides, oxides of manganese, etc., found in river water, there are other ways in which they may be absorbed from solution or precipitated on the sea bottom.

Anyone who has sailed along the Caucasian shore of the Black Sea will remember how sharply the colour of the sea water changes in the neighbourhood of Kolkhida, as the ship approaches Poti. The whole of the wide stretch of sea adjacent to the Kolkhida depression, and receiving its rivers, including the wide Rion and the small streams from the Poti swamps, assumes a yellowish-grey colour, and the water becomes muddy. But the most important feature of this change is the unusually sharp boundary between the translucent turquoise blue of the more distant part of the sea and the unattractive dirty strip near the shore. On a clear, sunny day with a calm sea, this boundary can be seen from afar, and the time taken by the ship to cross it can be determined with an accuracy of a few minutes. This long familiar phenomenon occurs at the mouth of every large river and is due to the fine silty particles carried down by the river. But since these particles are entering a medium with a greater salt concentration they are coagulated, *i.e.* they form large flocs and fall to the sea bottom. It appears that the strong current of fresh river water dilutes the sea in the neighbourhood of the delta and so lowers the salt concentration below the coagulation threshold, and the sharp boundary of the muddy water coincides exactly with this threshold.[1] Coagulation affects not only the suspended, but also the colloidal matter, and we must assume that in this way a certain amount of

[1] The waters of the Atlantic Ocean around New York are very dirty. This muddiness caused by the Hudson River is visible for a whole day before arrival in New York, but a sharp boundary is not observed.

silica may be precipitated as river water enters the sea and not absorbed by organisms. The same applies to the sesquioxides, oxides of manganese, and organic colloids.

In this way the sea bottom is covered, firstly, by the coarse water-borne material which settles with varying speeds under the influence of gravity; secondly, by the fine suspended and colloidal material which settles on coagulation; and thirdly, by material that is absorbed from solution in sea water by organisms and settles with their dead bodies and residues (shells, skeletons).

The distribution of this material on the sea bottom follows certain rules, and depends primarily on the distance from the shore and the depth of the sea, *i.e.* on geomorphological conditions.

As a matter of fact the material borne from the land is usually distributed according to the size of its mechanical elements: the farther from the shore and the deeper the water, the finer is the material deposited, and, vice-versa, the coarse-grained sands are deposited near the shore. It is evident that the deeper regions, which are incidentally more distant from land, have received only the finest clay, the amount of which (by weight) is considerably less than that of the skeletons and shells of the organisms living in the open sea and in its deeper parts. This circumstance makes it necessary in the classification of contemporary marine deposits to distinguish: (1) terrigenic, and (2) pelagic (deep water) deposits. The first occupies the shallow water and frequently extends to a depth of 2,000 m.; the second occupies the so-called abyssal regions of the sea bottom, which are rarely less than 1,000 m. deep. Terrigenic deposits are divided into two groups: (a) deposits of the shelf zone, and (b) deposits of continental muds. To group (a) belong the littoral deposits consisting of sea beaches, and also the sediments that stretch from the shore uninterruptedly over the whole of the *continental zone* (shelf). This zone reaches for some 200-250 km. into the sea and down to a depth of 200 m. The material forming the littoral deposits consists for the most part of the coarser mechanical fractions: pebbles, gravel, coarse and fine sand, but this does not exclude the possibility of clay material being present;

in fact, layers of this frequently alternate with the sands. The main factors determining the character of the littoral deposits are the composition of the rocks that form the sea-shore, the form of the shore, which determines the abrasive power of the waves, and the coastal currents capable of carrying away the comminuted material. The delta deposits in this coastal zone always form a special group which differ substantially in their mechanical composition from the other belts of littoral deposits. This applies still more to estuarine deposits in which fine silty material often occurs. The continental muds (b), consisting largely of alumino-silicic compounds, are varied (blue, green, grey muds), and their formation will be discussed later.

The deep-water muds also fall into two main groups: *organic oozes,* consisting predominantly of the remains of organisms (globerigina, radiolaria diatoms), and *red clay*,[1] which occupies the deepest parts of the ocean (from 4,000 m. downwards).

## 7. The Climatic Regions of the Hydrosphere

The scheme of the distribution of marine deposits just given does not, however, give a complete picture of their changes. It is, of course, broken in many cases when the deepening of the sea bottom does not correspond to the distance from the shore; it is considerably complicated by the interactions between the sediments, sea water and organisms mentioned above (p. 184) and which take place not only in the hydrosphere itself, but also on the sea bottom.[2]

[1] This deep-sea formation must not be confused with the red terrigenic mud.

[2] The alteration of minerals on the sea bottom is frequently known as *diagenesis*. Various authors, however, have used this word in very different senses. It was first introduced by Gumbel, who supposed that the crystalline schists are formed from marine sediments and referred to their formation as diagenesis. He considered that this process was concomitant with the deposition of the sediment or followed immediately after. Subsequent authors have altered the meaning of the term to the process of cementation and consolidation of sediments (Walther, Lapparent). Diagenesis, in this sense, may be applied to the processes occurring in the sedimentary rocks on land. Other authors, however (Haug, for example) connect diagenesis exclusively with the submarine regions. And, finally, A. E. Fersman limits diagenesis exclusively to processes occurring on the *surface of the sea-floor* (*cf.* Geochemistry of Russia), excluding at once cementation and consolidation. In view of such diversity in the application of this term we shall not use it.

The character and distribution of these reactions become clearer if we remember that the hydrosphere is not a completely homogeneous medium, and that within it and on the sea floor there occur different "climatic" regions and provinces. As in the case of subaerial climates, temperature is one of the most fundamental factors in characterizing the climates of the hydrosphere.

In place of humidity, which is of great importance in the grouping of subaerial climates, the content of dissolved air and carbon dioxide can be used in the subdivision of marine climates. If to these two factors we add the degree of penetration of light and changes in pressure, we define the most important elements of *hydroclimates* on which depend the intensity of the processes of submarine weathering and the distribution of organic life and biochemical processes.

Taking into account all these factors we may distinguish, first of all, the surface portion of the ocean to a depth of approximately 200 m. Sufficient sunlight usually penetrates to this depth, and the temperature is influenced to a great extent by solar radiation. The existence of chlorophyll-bearing plants is directly dependent on the amount of light and consequently so are photosynthesis and its corollaries—the evolution and absorption of carbon dioxide and oxygen. On the basis of temperature this zone may be subdivided into thermal belts. At the present time it can be divided into three at the most: two cold, confined to the southern and northern polar and subpolar latitudes; and a warm, in the tropical and subtropical regions. In cold seas the content of oxygen and carbon dioxide increases, with the result that the stability of $CaCO_3$ decreases. Under such conditions organisms with calcareous shells and skeletons cannot be widespread. The low evaporation leads to a decrease in salinity, which in its turn lessens the coagulative power of the water for silty and colloidal particles. There is thus an increase in the numbers of organisms rich in siliceous materials. In warm seas, on the other hand, carbon dioxide cannot be held for long, and the absorption of lime by organisms for the construction of their hard parts is wide-

spread. It is obvious that this will be reflected in the deposits on the sea bottom.

In addition to temperature, light and dissolved gases, the conditions under which the different organisms can exist is determined by the proximity of land and the sea bottom. We must thus recognize the shallow-water region, and the pelagic region which includes the deeper parts of the oceans. The animals in the pelagic region are of the most diverse types, but those that are devoid of the power of locomotion, either active or passive, and so lead a sedentary life, are absent. But there are specific examples of pelagic fauna living far from shallow water and coasts (whales; certain molluscs, predominantly of the *Cephalopoda;* a few genera of worms; individual species of *Cœlenterata, e.g. Stenophora, Siphonophora*). Rhizopods are especially active in the pelagic region. In warm seas they are represented by globigerinæ with their calcareous shells, while in cold waters forms with siliceous skeletons predominate. Algæ are also widely diffused in the pelagic region, and again the calcareous varieties predominate in the warm, and the siliceous (diatoms) in the cold waters. It may be mentioned here that the subpolar seas are, in general, distinguished by a much richer fauna and flora than the tropical. The abundance of dissolved air, the presence of silty matter and the lower salinity of the northern seas form much more suitable conditions for organic life than the tropical, which are poor in oxygen, and much more saline.

A complete contrast to the conditions in the surface portion of the hydrosphere is provided by the more uniform *abyssal* region of the ocean, which includes all depths below the 1,500-2,000 m. isobaths. In this region the temperature is unusually constant, and varies at the most within a very narrow range ($-0{\cdot}5°$ to $+4°$). Such a low temperature over all the deeper portions of the ocean, not excluding tropical seas, is explained by the inflow of cold water from subpolar latitudes due to convection currents set up by temperature variations in the surface, and to loss of water by evaporation. Sunlight does not penetrate, and the only illumination in these icy deeps is that from the luminous organs of certain

deep-water animals. It is obvious that chlorophyll-bearing plants cannot occur here; and, in general, no plants, with the possible exception of bacteria, are found. Life becomes poorer and poorer with increasing depth, and the abyssal regions of the sea bottom may be likened to deserts. Nevertheless, they cannot be regarded as absolutely devoid of life, and individual representatives of the animal kingdom are encountered even at the greatest depths. Deep-sea fishes have been taken at depths of 4,000 m. (representatives of the *Stomidæ, Macruridæ,* etc.); many crustaceæ—certain crabs, peculiar shrimps from a depth of 6,000 m.; from the same depth come the hermit-crayfish, which still continues its cohabitation with the sea-anemone (*Pagurus abyssorum*). *Echinodermata,* and especially starfish and sea-serpents, siliceous sponges, which, although usually confined to depths of 200-1,000 m., are all found down to 6,000 m. But most characteristic of the abyssal region are specific forms of radiolaria which inhabit the depths from 4,000 to 8,000 m.

The middle position between the surface and abyssal parts of the ocean is occupied by the *bathyal* region, at depths between 200 and 1,500 m. Sunlight penetrates, although weakly, into the upper part of the bathyal region, and members of the vegetable kingdom may be found there. The calcareous algæ (species of *Lithophyllum* and *Lithothamnia*) penetrate to the greatest depth since they are satisfied with only feeble illumination. The vast deeper-lying parts are inhabited mostly by members of the animal world. In places the fauna of the bathyal region may be fairly rich and diverse. In contrast to the more or less constant temperature of the abyssal region, the temperature of the bathyal zone varies somewhat, and it is necessary to distinguish a cold and a warm zone, at least, but in each of these zones it is fairly constant, and only reflects to a slight extent the seasonal variations that are characteristic of the upper part of the hydrosphere. Owing to the low oxygen content of the water of the warm bathyal region, the organic remains that fall to the bottom undergo, for the most part, putrefaction. The process of desulphofication is likewise very active. As a result of these reduction react-

ions, compounds of iron are altered to the colloidal mineral troilite (p. 100), and continental (terrigenic) muds assume a dark colour. On the crystallization of troilite and its change to pyrites, these become blue. This is the origin of the marine hydrotroilite muds, found adjoining the continents to a depth of 200 to 3,000 m. (and sometimes below 5,000 m.). To this group belong the "blue muds" already described. Of the same origin is the dark mud of the Black Sea, the Caspian Sea and other marine basins both open and closed. Over the greater part of their area these muds contain calcareous shells and the residues from plankton and the inhabitants of the sea bottom. The investigation of samples of blue muds collected by the *Challenger* expedition showed that on the average it contains 12·5% calcareous shells, and 3·3% siliceous skeletons, the remainder being fine silty material (*ca.* 60%) and coarser material (over 20%). The stability of the calcareous residues in the blue and other hydrotroilite muds confirms the extremely low content of dissolved carbon dioxide in the water. The presence in these muds of iron sulphide, hydrogen sulphide and calcium carbonate together deserves special consideration since it has its consequences in the further transformation of these muds. It should be noted that the hydrotroilite muds of the bathyal or deeper regions of the sea have their analogues in the sediments of the lacustrine-estuarine phase of the shallow sea; these are the black sapropels that are frequently of therapeutic value.

As would be expected, the blue mud, when we pass to the subpolar bathyal regions, gradually decreases in area and gives place to the grey variety, which differs but little from the similar sediments of the littoral zone. An abundance of dissolved oxygen does not allow the extensive development of reducing processes, and the coarse material dropped by floating ice when it melts and breaks up, makes this grey mud still more like the coastal sediments, even where the sea is quite deep. In addition to the blue and grey muds, there is still another form of terrigenic sediment that is fairly widely diffused. This is the green *glauconitic mud and sand*. The green mud occurs between the 200 and 1,800 m.

isobaths. It was found between these depths in the Atlantic Ocean along the shores of N. America, Portugal and the western coast of Africa; in the Indian Ocean along the eastern shores of Africa; off Western Australia; and in the Pacific along the coasts of Japan and the western shore of N. America. It has been observed that opposite the estuaries of large rivers these belts of green muds are broken. In places the blue mud directly adjoins the green, and there appears to be some relation between them. Frequently glauconitic formations in the form of kernels filling tests occur in samples taken from the blue mud. It is possible that the regions of green mud are connected with an abundant precipitation of ferrosilicic coagels derived from the solutions of silica and ferrous iron characteristic of the alkaline medium of the blue mud. The crystallization of these coagels results in the formation of glauconite. There is reason to believe that in the green mud there is an increase in the stability of siliceous skeletons, the content of which reaches 13·6%. There are also a number of local terrigenic muds, as, for example, volcanic muds surrounding islands of volcanic origin, coral muds, and deposits from great rivers borne far into the sea. Opposite the mouth of the Amazon there occurs a peculiar red mud formed of the allitic products of weathering carried by that river. The yellow silt of the China Sea is borne from the loess by the rivers.

The most important forms of deep-water organic sediments characteristic of the abyssal regions of the sea bottom are the *globigerina* and *diatom oozes*, and, in spite of the uniformity of conditions on the abyssal floor, these deposits are fairly well delimited. Globigerina ooze occupies an enormous area in the Atlantic Ocean from 700 to 5,000 m., a considerable part of the Indian Ocean, and the southern part of the Pacific, and being mostly confined to sub-tropical latitudes, it gradually gives way to diatom ooze in the subpolar regions. The latter ooze covers a large area in the Antarctic Ocean and the northern parts of the Pacific.[1]

[1] The Arctic Ocean and the northern parts of the Atlantic are in general devoid of deep-water deposits, and their comparatively shallow bottom is covered by terrigenic sediments.

The principal constituents of globigerina ooze are the calcareous tests of *pelagic* foraminifera, the most conspicuous being those of *Globigerina*. Besides these there are many fragments of other marine animals which possess hard parts along with coccoliths and rhabdoliths—fragments of minute calcareous algæ. We thus see that globigerina ooze consists predominantly of the remains of organisms living, not in the ooze itself or in the adjacent waters, but much nearer the surface of the ocean in a belt that is characterized by extremely different hydrothermal conditions. It must be noted that the composition of globigerina ooze fairly clearly reflects all the changes occurring in the upper pelagic shell. Thus, in tropical regions the tests in the ooze become larger and reach a size visible by the naked eye, while on approaching the cooler latitudes they decrease to microscopic size, becoming thinner and more delicate.

But the waters of the abyssal region are not suitable for the preservation of calcareous shells, which with any abundance of carbon dioxide will dissolve, so that the presence of globigerina ooze in this region must be explained by the fact that *the amount of material falling from the surface in the form of $CaCO_3$ exceeds the loss by solution.*

This explanation is confirmed to some extent by the fact that the greatest depths (over 4,000 m.) are almost devoid of globigerina ooze, since to reach this depth the calcareous shells have to travel a long distance through extremely unfavourable conditions. The deposits in these parts consist of the material left after the dissolution of the carbonate, with minerals of other origin. The regions of deep-water red clays into which the globigerina ooze gradually passes, occupy extensive areas of the deepest parts of the Pacific and Atlantic Oceans, and occur predominantly in the eastern part of the Indian Ocean. The main mass of red clay (90%) consists of fine particles of mineral clay, and only about 10% consists of calcareous and siliceous skeletons. The amount of $CaCO_3$, however, changes very definitely with depth. Thus, according to the analyses of samples collected by the *Challenger* expedition, red clay at 3,600-4,500 m. contains on the average 8·4% at $CaCO_3$, at 4,500-

5,500 m. 7·2%, and a depth of 5,500-6,400 m. only 0·88%. Apart from the aluminosilicate systems, the nature and composition of which have been little investigated, there occur also hydrated oxides of iron and manganese, phosphates of calcium, volcanic minerals (*e.g.* phillipsite and other zeolites), and fragments of rock. This material is partly supplied by submarine volcanic ejectamenta, and to some extent consists of the finest and most easily dispersed particles of terrigenic origin, the insoluble residues of pelagic material and atmospheric and cosmic dust that has fallen into the sea. It may be assumed that the cold and less saline currents bring colloidally dispersed aluminosilicic and iron-manganese salts, and also dissolved carbonates of iron and manganese which, owing to the increase in salinity at this point, are coagulated and settle to the bottom. The precipitation of gels in this region, in any case, can be taken as fully established, since the bones of marine animals occurring here are often covered by a characteristic colloidal film of hydrated oxides of iron and manganese.

Turning to the diatom ooze, whose distribution requires no explanation, it is necessary to note the peculiarities of its chemical composition, viz., the insignificant amount of material insoluble in hydrochloric acid (*ca.* 5%) and the low iron content. The first of these facts indicates that aluminosilicates are here almost completely decomposed, and the second supports our suggestion that hydrated iron oxides in cold seas are more or less easily dissolved or dispersed and carried away by currents to be deposited in the red clay regions.

In addition to the above types of deep-sea sediments, we must mention *radiolarian* ooze, which may be regarded as a phase of the red clay enriched with siliceous, and especially radiolarian, skeletons; and *pteropod* ooze into which globigerina ooze passes in tropical latitudes. Pteropod oozes are rich in the tests of molluscs of *Pteropoda* and *Heteropoda* groups.

Just as the great physiographical regions on land must be subdivided depending on the structure of the surface, the direction and nature of winds, etc., so the hydrosphere has

its own provinces of different origin and extent. These are created by marine currents, the peculiar conditions in closed seas which are far from the oceans, *e.g.* the Mediterranean, and, finally, by the very complicated structure of the surface of the sea-floor, the rise and fall of which is somehow or other reflected in the direction of currents and the variations in temperature.[1] All this, of course, is reflected in the nature and distribution of the sediments, and the relationships shown are only an outline of a much more complicated and, to a great extent, unknown reality.

### 8. Secondary Cycles of Continental Weathering. Forms of Paraeluvium and its Concomitant Accumulations. Forms of Red-Coloured Eluvium. Heterogeneous Deposits.

All marine sediments undergo alteration as they are buried and consolidated, but still more fundamental changes take place in them during the processes of mountain building or, in general, during the vertical and horizontal transposition of the earth's crust. As a result of such movements these deposits rise clear of their aqueous covering, and in the shape of more or less metamorphosed sediments form some or other land mass. In a great number of cases we can easily decide from which type of marine deposit the contemporaneous sedimentary rocks of the land originated. In conglomerates, sandstones, many clays and shales we discern types of the littoral (coastal) zone; in the dark calcareous clays we find indications of the blue mud; in cherts, sediments rich in siliceous skeletons; in glauconitic sands and clays, the green mud, and finally, the type of the marine sediment is especially easily discerned in the various kinds of limestone, rich in well-preserved remains of calcareous skeletons. But it must be admitted that up to the present, no examples are known of sedimentary rocks that have indubitably been formed from the abyssal red clay and its adjacent deep-water phase, globigerina ooze. At one time it was supposed that chalk

[1] A classical example is to be found in the Wyville Thomson barrier, which sharply separates the cold northern part of the Atlantic Ocean from the southern, warmer, part.

was an example of such a deep-water sediment, but the careful investigations of Cayeux showed the predominance of bottom (benthal) organisms, which are more characteristic of the bathyal depths, in its formation. This circumstance has given certain geologists grounds for regarding the distribution of the abyssal depths as unaltered throughout the whole age of the earth. But it is possible, however, to suppose that the deepest deposits undergo such radical changes during their slow and complex uplift from the sea, that to determine the connexion of such highly metamorphosed rocks with the deposits from which they originated is impossible in the present state of our knowledge.

The massifs of sedimentary rocks, in the form of upland plateaux or even mountain ranges and ridges, are dissected by erosion, and on their surface arises a system of watersheds. On these there again begins the accumulation of residual material and the migration of the more mobile products of weathering under the influence of weathering and denudation. In this way we have a second, or rather secondary, cycle of distribution of the products of weathering and the formation of residual and accumulative forms of the crust of weathering. If the sedimentary rocks have first of all undergone such strong metamorphism that no vadose minerals remain, that they appear as crystalline schists (micaceous schist, phyllite, chlorite schist, etc.), then the new cycle of weathering and the distribution of its products differs in no way from that previously considered. These rocks when metamorphosed are, as it were, reborn, and have arrived at a state very close to primary igneous rocks. The residual and accumulative products of weathering, both in nature and form, will differ very little from those described for primary rocks, and for their eluvium we retain the name orthoeluvium.

The weathering of little metamorphosed sedimentary rocks that still retain vadose minerals is somewhat different. In such cases the processes of subaerial weathering again attack the vadose minerals that have already passed through a series of changes in the crust of weathering, and the residual products of such rocks we shall call *paraeluvium*. It is evident that the paraeluvium of watersheds must also

have its related forms in the accumulative crust of weathering on depressed elements of relief in the same way as orthoeluvium. Nevertheless, the character of paraeluvium itself and the distribution of the accumulative forms will depend to a considerable extent on the nature of the sedimentary rocks.

In this connexion, sedimentary rocks may be divided into three main groups: (1) *aluminosilicic,* into which fall all with a predominance of vadose aluminosilicic minerals, viz., clays, shales, slates, glauconitic sands and clays, etc.;[1] (2) *siliceous, i.e.* with a definite preponderance of minerals corresponding in composition to dehydrated and hydrated silica: quartz sands, and sandstones, quartzites, grits, etc.; and (3) *calcareous, e.g.* marls and the various limestones.

The detrital stage of the paraeluvium of aluminosiliceous sedimentary rocks is in many cases only slightly developed or is absent altogether. Only the very compact rocks of this group (slates) give a more or less definite detrital eluvium. The calcareous phase is, in general, possible only for the rocks that are fairly rich in bases. But the majority of clays and shales are poor in bases, and so this phase is here even more weakly developed than that in acid igneous rocks. The shales of the south Crimean coast, for example, do not yield the calcareous phase even under extremely favourable conditions (east of Alupka), under which the colluvium from the Jurassic limestones is long preserved unleached. It is obvious that the phase of acid siallitic paraeluvium in clays and shales can be well developed under any climatic conditions. And there seems to be nothing to prevent the formation of the allitic stage under the appropriate conditions of time and place. Nevertheless, no trustworthy example of allitic eluvium on clays, shales, or similar rocks can be given. Harrassowitz concluded that on clays there only occur weak indications of lateritic weathering.[2] We may, with sufficient accuracy, assume that the reasons for the weak laterization of clays are not to be found in their composition, but in the historico-geological and geomorphological conditions. Indeed, since they appear in the majority

[1] Arkoses, conglomerates, and other products of the coarse disintegration of igneous rocks, may be regarded as the detrital stage of orthoeluvium.

[2] "Laterit," pp. 373-376. *Cf.* J. B. Harrison, Katamorphism of Igneous Rocks, *Imper. Bur. Soil Sci.,* 1934.

of cases as young rocks and do not always occur on the main watersheds of ancient land, the conditions are not favourable to the development of the allitic process, and so the appropriate phases are not reached. But the possibility of this development still remains, and this is supported by cases of the laterization of rocks derived from them by metamorphism.

It is evident that the composition of drifts, *i.e.* the accumulative crusts of weathering, covering the slopes and depressions on the massif of sedimentary rocks, is dependent on the paraeluvium of the watersheds, and if the sedimentary rocks consist of clays and shales poor in chlorine, sulphur and bases, then the calcareous and chloride-sulphate accumulations are either undeveloped or appear in weakly or badly expressed forms.

Still poorer and more restricted forms of paraeluvium and their related drifts are those formed from highly silicic rocks containing only negligible amounts of primary and secondary alumino-siliceous cement. Thus, quartz sands or sandstones with a siliceous cement yield homogeneous forms of paraeluvium and its concomitant drifts that are loose sandy deposits. The quartz sands containing calcium carbonate or chlorides and sulphates may be referred either to the *heterogeneous accumulations* to be described below, or to those in which the initial sedimentary rock contained a considerable admixture of minerals other than quartz.

The great diversity of the third category of calcareous rocks depends both on the nature of the changes undergone by them during their sedimentation, and on the subsequent metamorphism. Marly clays and any other Pontic limestone, for example, in which the shells are visible to the naked eye, consist of little-changed sedimentary rocks, while the compact Jurassic crystalline limestones composing the highest ridges of the mountainous part of the Crimea are fairly highly metamorphosed.[1]

[1] It must be noted that among igneous rocks there are varieties containing $CaCO_3$. Their eluvium, and that of highly metamorphosed (crystalline) limestones, strictly speaking, ought to be considered orthoeluvium. But since the area of sedimentary calcareous rocks is so much greater than that of the primary varieties, it seemed to be more convenient to describe the products of the weathering of calcareous rocks in general under the derivatives of paraeluvium.

Correspondingly, in certain cases the stage of detrital eluvium is fairly well developed, while in others it is hardly formed at all, but, for obvious reasons, the stages of detrital and calcareous eluvium merge into one common phase in all cases, since the accumulation of lime has already taken place in the rock itself. Weathering will thus take the form of the solution and leaching of the carbonate only, and the formation, in this way, of *siallitic supra-calcareous paraeluvium*. The presence of these residual products is due to the fact that limestones usually contain, in addition to calcium carbonate, an admixture of other minerals: in particular aluminosilicic and iron compounds. In considering the forms of limestone eluvium we encounter one formation that is still not fully explained. In the Karst region (*i.e.* the carbonate plateau that stretches to the south of the valleys of the Isonzo, Idria and Sava, and occupies the western part of Carniola to Istria) the upper surface horizons of the limestones are covered with a red-coloured crust known as *terra rossa*. This term has subsequently been applied to all red clay formations overlying calcareous rocks, and, by certain workers, to those that have been observed over non-calcareous rocks. The innumerable hypotheses advanced for the origin of terra rossa, frequently based on fully trustworthy material, are, nevertheless, very divergent. This has happened because under this name there are grouped very different, and not always even eluvial, formations, the guiding principle being one feature: the red colour. It is natural that the results of the study of one or several red-coloured formations must not be applied to all of them.[1]

The cause of the red colour of laterites and of many siallitic sedimentary rocks, and of sands and sandstones, is by no means yet decided. It is quite natural to suppose that it is connected with some form or other of hydrated iron oxide, but just with which and what the conditions of formation are, we do not know. In appraising these phenomena it is necessary to take into consideration the following facts:—

[1] The work of Reifenberg on the red-coloured products of weathering in the neighbourhood of Jerusalem is characteristic of this standpoint. *Kolloidchemische Beihefte*, 1929, **28**, H. 3-6.

(1) The products of allitic weathering are by no means always red coloured, and although the conception of laterite is associated with its red colour, it should be said that allitic products of weathering are not restricted to laterite.

(2) The products of the weathering of limestones even in the Mediterranean region, to which the development of terra rossa is restricted, are by no means always red. In this connexion an instructive example is provided by the Jurassic and Cretaceous limestones of the Southern Crimea. Whilst the first are covered with a red-coloured crust, the second are mantled with a grey or yellowish-grey crust of weathering (Baïdar valley).[1]

(3) The red-coloured siallitic crust of weathering of calcareous rocks is frequently found far from the Mediterranean or tropical and subtropical regions. It is only necessary to point to the red weathered material formed from the calcareous rocks in the Lenigrad region.

(4) Red coloured products of weathering from alumino-silicic (non-calcareous) rocks are often found in subtropical and Mediterranean regions. They show all stages, residual and accumulative, *i.e.* they become enriched with carbonates, chlorides and sulphates (the deserts and semi-deserts of Arabia, Algeria and the steppes of the Pyrenean peninsula). In other places they show the siallitic unsaturated phase (the Algerian mountains), and finally in yet other regions the allitic phase in the forms of laterite.

In this way it is obvious that the question of red colour of eluvial accumulative drifts ought to be regarded as independent of the various phases and forms of the crust of weathering that we have formulated.[2]

Returning to the siallitic paraeluvium of calcareous rocks, it should be said that this phase, other conditions being equal, ought to be more stable than the siallitic ortho-eluvium or paraeluvium of aluminosilicic rocks. Indeed, during the weathering of limestone, the products are in con-

[1] It should be noted that our observations show that the contemporaneous products of weathering of the Jurassic limestones in mountainous Crimea are not red coloured.

[2] Certain writers consider even terra-rossa to be formed quite independently of the underlying limestone (Taramelli, Schiere, J. Walther, von Leiningen, *et al.*).

stant contact with a solution of calcium, and sometimes also magnesium, salts, which results in the aluminosilicic adsorption complex of the residual material being completely saturated with these bases. The complex is then in a stable state. It is possible that it is just this circumstance that prevents the formation of the allitic phase of weathering on limestones. Harrassowitz noted only "allitic-siallitic" forms on these rocks.[1]

Among the accumulative forms associated with the paraeluvium of calcareous rocks the calcareous stage is well provided for and is apparent even under conditions of a moist climate, as can be observed on the lower marine terrace of Abkhazia, which receives the calcareous material from the neighbouring mountains. The development, to any extent, of chloride-sulphate accumulations depends on the composition of the limestone.

Actually, however, negative land forms very often obtain their material from the diverse rocks forming the plateaux, mountains and other relatively elevated areas. Frequently, therefore, the products of the weathering of other rocks become intermingled with the material originating on any watershed and lead to the formation of heterogeneous drifts in which the various phases of the accumulative crust of weathering may be indistinguishable or alternate in different ways. The alluvium of large rivers is an especially characteristic form of such heterogeneous rocks.

Thus, in the middle reaches of the Don (U.S.S.R.) its present valley in many places obtains its material both from quartz sands devoid of $CaCO_3$, which form the high terrace, and from the loess of the watersheds in which the ravines and valleys of the younger rivers of the Don system are being cut. Among the sediments in the present Don Valley and its tributaries we may frequently observe sands enriched with $CaCO_3$.[2]

Of much more homogeneous composition in this connexion are the colluvial and proluvial deposits, but even they, in certain cases, may give forms of heterogeneous ac-

[1] *Loc. cit.*
[2] See the author's work on the Don Sands.

cumulations, as, for example, when the mountain summit consists of rocks different from those at the base. Such colluvium is widespread along the southern coast of the Crimea, where the weathered material from the limestones forming the mountain summits commingles on the lower slopes with that from the shales and slates.

### 9. Weathering Cycles of the Third Order. Neoeluvium and its Forms

Movements of the earth's crust embrace not only the regions occupied by marine basins, but also a considerable part of the land surface. Recently there have been more and more demonstrations that the movement of the earth's crust took place not only during Tertiary and earlier times, but also more recently, and is still occurring even at the present time. To the data confirming this attitude, made mostly in coastal regions (coasts of Scandinavia, Italy, Black Sea coast of the Caucasus, etc.), it will not be superfluous to add some facts concerning regions much farther from the sea. Thus, a fairly considerable movement was observed by K. A. Prokopov in the loess now covering the hills broken by the Khankab fault, south of the town of Grozny.[1] Apparently of the same origin is the watershed between Western and Eastern Manych. There existed in post-tertiary times the Manych strait between the Black and Caspian Seas, but this is now cut by a watershed so that the rivers run in opposite directions. Such a movement is observed at present in the middle reaches of the River Sala, where its channel has cut much more deeply into the drifts than it has done in its upper course.[2] All these facts show that not only sedimentary rocks of considerable age, but also post-tertiary drifts, may, under definite conditions, be uplifted to occupy the watershed position. It follows, therefore, that at a certain moment typical eluvial processes may arise even on the accumulative crust of weathering, with the accumulation of residual and the migration of the mobile products of weathering. We thus have the most recent *third*

[1] *Trans. Geol. Comm.*, n.s., Pt. 134, 1922 (Petrograd).
[2] Personal observation by the author in 1928 (unpublished).

*cycle* of the redistribution of the products of weathering with its new centres. The corresponding eluvium which has, as we shall see, quite peculiar forms, we shall call *neoeluvium*.

The direct formation of neoeluvium on sediments depends, obviously, not on tectonic movements, but on the dissection of the drifts and the creation of new watersheds of varying sizes. Such large rivers as the Volga, Don and Dnieper and their tributaries cut the loess into great watershed massifs, and the complex network of ravines, gullies and hollows, in the mezzo- and micro-relief of these watersheds results in an infinite number of large and small areas isolated one from the other. The tops of these new elements of relief are no longer influenced by lateral movement of material, and begin to lose their own mobile products of weathering. Such elements are the centres of the formation of neoeluvium.

It is evident that among the forms of neoeluvium there will be a number analogous to ortho- and para-eluvium, with the restriction that the young neoeluvial processes give forms that are usually not very different from the initial material. No examples of a calcareous drift yielding an allitic neoeluvium are known. Nevertheless on a siallitic drift that already contains allitic material contaminated with fortuitous aluminosilicic systems, the removal of the latter may easily lead to the formation of allitic neoeluvium. The formation of siallitic neoeluvium on the calcareous accumulative crust of weathering is very common. It can be observed over vast areas of the south Russian loess, the upper horizons of which, on elevated positions, are already devoid of $CaCO_3$, while the lower layers show considerable accumulations of that salt.

There is no doubt that this removal is connected with the redistribution of $CaCO_3$ within the more restricted limits of the calcareous accumulative crust of weathering. The resulting siallitic neoeluvium, just like the supra-calcareous paraeluvium, passes through various phases. It becomes freed from calcium carbonate, but still retains calcium and other metallic cations in the adsorption complex. Subsequently, the action of carbonated atmospheric water leads to

the loss of the adsorbed ions and their replacement by hydrogen, with the formation of an acid medium. These stages can be observed under the most diverse conditions. Thus, there may be seen in the Pskov region the fully saturated neoeluvium of a calcareous moraine, while many examples of the formation of unsaturated neoeluvium on calcareous loess are known in the Ukrainian forest steppe.

A quite unique form of neoeluvium arises from the chloride-sulphate accumulative crust of weathering when this occurs on a watershed, and it is effected both on a large and small scale. The fairly extensive plateau of Ust-urt consists of a region sometime consisting of chloride-sulphate accumulations, but now, as a result of the sinking of the adjacent areas, forming a plateau, eluvial processes have begun on its surface. Leaching is slow because the rainfall is very low and the area not deeply dissected. Certain parts of the Precaspian basin show similar features. The colloidal material in these chloride-sulphate accumulative forms is generally saturated with sodium, and since sodium clays are highly dispersed there is usually a downward movement of fine material as leaching proceeds. When this encounters the lower lime deposits it becomes coagulated and the corresponding horizon becomes exceedingly compact. Neoeluvium containing such compact horizons represents a form of *solonetzous neoeluvium*.

But cases may exist in which the saline neoeluvium is devoid of such formations.

Let us imagine a chloride-sulphate drift in which sulphates predominate and which has developed, as is usual with continental salinization, on a calcareous drift.

In this case the conditions are favourable for the formation of calcium sulphate :—

$$[SiAl \ldots 2OH']Ca'' + Na_2SO_4 \rightarrow [SiAl \ldots 2OH']_2Na' + CaSO_4$$

and $Na_2SO_4 + CaCO_3 \rightarrow Na_2CO_3 + CaSO_4$.

But a great accumulation of $CaSO_4$, which is less soluble than NaCl and $Na_2SO_4$, means that when these salts are lost by leaching the adsorption complex will be kept satur-

ated with calcium, and so the formation of systems, such as [SiAl . . . OH′]Na˙, will be prevented. The induration of the lower horizons due to the precipitation of colloids carried down from the surface will also be absent. This second form of saline neoeluvium, rich in gypsum, is common on many terraces and plateaux that are now undergoing desalinization.

## 10. Conclusion

We have now seen that the distribution of the products of weathering on land surfaces is determined by three main cycles: (1) orthoeluvium, (2) paraeluvium, and (3) neoeluvium. With these are connected various accumulative phases, and the whole may be represented as follows:—

*1st Cycle*

| *Phases of Orthoeluvium.* | *Derived Accumulations.* |
|---|---|
| 1. Detrital. | 1. Clastic drifts. |
| 2. Calcareous. | 2. Chloride-sulphate. |
| 3. Siallitic. | 3. (a) Calcareous<br>(b) Chloride-sulphate. |
| 4. Allitic. | 4. (a) Siallitic (allophanic).<br>(b) Calcareous.<br>(c) Chloride-sulphate. |

*2nd Cycle*

| *Phases of Paraeluvium.* | *Derived Accumulations.* |
|---|---|
| 1. Detrital.<br>Detrital (from calcareous rocks).<br>Calcareous. | 1. Chloride-sulphate. |
| 2. Siallitic.<br>Siallitic supracalcareous. | 2. (a) Calcareous.<br>(b) Chloride-sulphate. |
| 3. Allitic (?). | 3. (a) Siallitic.<br>(b) Calcareous.<br>(c) Chloride-sulphate. |

*3rd Cycle*

| *Forms of Neoeluvium.* | *Derived Accumulations.* |
|---|---|
| 1. Saline solonetzous. Saline gypsum-bearing. | 1. Intensification of chloride-sulphate accumulation within the chloride-sulphate crust of weathering. |
| 2. Leached supracalcareous (siallitic). | 2. Intensification of $CaCO_3$ accumulation within the calcareous crust of weathering. |
| 3. Unsaturated siallitic. | 3. Increase in amount of alumino- and ferri-siliceous systems within the siallitic crust of weathering. |

The unceasing action of these three cycles predetermines the general outline of the distribution of the products of weathering, but a deeper study shows that within each phase of eluviation and accumulation there occurs an internal movement of the products. This is brought about by the activity of organisms and organic compounds. All these movements are closely connected with the process of soil formation which occurs in various guises under the most diverse conditions on ortho-, para- and neoeluvium as well as on their associated accumulations. The migration of the mobile products of weathering may be hindered in certain cases (eluvium) by the development of organic life, and especially vegetation, on the surface. The mobile products are absorbed and utilized by the organisms and the composition of the residual mass becomes fundamentally altered, most of all in the surface layers where the organic residues accumulate — the so-called humus horizons. In other cases (accumulations) the abundance of incoming material may depress the soil forming processes which may be only feebly expressed (solonchaks). But in all cases it introduces certain more or less fundamental changes in the development of the crust of weathering and frequently results in the formation of quite new mobile compounds,

which in their turn may give rise to new deposits, *e.g.* ferrihumate sols and coagels, and the lacustrine and bog iron ore formed by them. On the other hand, soil-forming processes are by no means independent of the weathering and transport of material already considered. Occurring as they do with an abundant evolution of carbon dioxide, which is included directly in the carbon, nitrogen and oxygen cycles, they intensify weathering and take an active part in the formation of the residual and mobile products. The discussion of these processes is too great a theme to be contained even in a chapter and will, therefore, form a sequel to this book.

# APPENDIX

## Note on the Structure of Silicates

The older structural formulæ given to silicates were based on the assumption that these compounds resembled the ordinary chemical salts. Of all the suggestions put forward that of Vernadsky was the only one to explain satisfactorily many of the geochemical properties of the various silicates. The development of Werner's co-ordination theory led to various attempts to apply it to silicates. Jakob (**7**) made a fairly complete application but his formulation did not completely satisfy known facts. Wahl (**14**) in a series of papers compared the aluminosilicates with alumino-oxalates, and showed that aluminium must have sixfold co-ordination valency. Wahl gives a number of structural formulæ, but some of these do not agree with more recent X-ray determinations, and they are essentially different from those proposed by Jakob. Not until the X-ray method of studying crystal structure was developed was any real progress made in the elucidation of the constitution of the complicated series of silicates and aluminosilicates. Optical methods developed by Marshall (**9**) have kept pace with the X-ray work, and have proved of great value in cases where the X-ray method has not been conclusive.

Nevertheless, the application of these structures even to the commoner geochemical problems is only just beginning. Notable contributions have been made by Goldschmidt (**5**), and a very interesting summary of the application to certain geological problems has been given by Brammall (**2**). Little attention seems to have been devoted to the consideration of weathering problems, such as are discussed in this book, and in particular to the correlation of the results of the newer investigations with Vernadsky's formulation of the silicates.

A number of excellent summaries of the X-ray work on the constitution of silicates have been published, among which may be mentioned that of W. L. Bragg (**1**) and that of Hassel (**6**). These should be consulted for full details.

The fundamental unit of all silicates and aluminosilicates has been shown to be the silicon-oxygen tetahedron $SiO_4^{4-}$, which occurs as an independent group in the orthosilicates (*e.g.* olivine) or is combined into sheets, chains or three-dimensional networks as in the more complex minerals. The other constituents may be co-ordinated to the Si-O frameworks, may replace part of the silicon, or occur as independent groups.

The study of the clay minerals made by American workers has provided results which have an interesting bearing on Vernadsky's theory. Pauling (**10**) has shown that the fundamental bricks of these minerals are :—

(1) Silicon layer—$Si_2O_3(OH)_2$ or multiples.

(2) Aluminium layer—$Al_2(OH)_6$ or multiples.

(3) Magnesium layer—$Mg_2(OH)_4$ or multiples.

Taking the kaolinite-halloysite group as an example we have the following arrangement of the first two groups in halloysite :—

$$O_3.Si_2(OH)_2.Al_2(OH)_6.$$

The empirical formula is then $2SiO_3.Al_2O_3.4H_2O$. If the 8(OH) groups are condensed to $(OH)_4$, two molecules of water are set free and two O-ions become available for linking up the two sheets, and we obtain :—

$$O_3.Si_2.O_2.Al_2(OH)_4.$$

The summation of this structure gives $2SiO_2.Al_2O_3.2H_2O$, the empirical formula of kaolinite. The interesting point about the above structure is that the two layers are bound by two electro-valencies which will hold the layers tightly together and the resulting structure will be very stable. In this way the ring structure postulated by Vernadsky is not required. In halloysite the layers are neutral, being held together by secondary forces. They are thus easily forced apart by water molecules. According to Edelman (**4**) the H of the OH groups attached to the silicon

in halloysite is replaceable by bases, thus reconciling the old "hydrated aluminosilicic acid" theory with the newer results. See Brammall (**3**).

Ross and Kerr (**12**) have shown that halloysite may pass over into kaolinite naturally and that both are products of normal weathering.

Pauling's studies (later confirmed and extended) have shown that the structures of a large number of platy minerals, including the micas and chlorites, are likewise built up from these fundamental units with certain replacements, *e.g.* $Si^{4+}$ by $Al^{3+}$, $Al^{3+}$ by $Mg^{2+}$. Such replacements leave the framework with either an excess positive or negative charge which is made up by the incorporation of a cation, or anion, *e.g.* K or OH. The structure of muscovite is as follows:—

$$K_2.O_6.Si_3Al.O_4(OH)_2.Al_4.O_4(OH)_2.Si_3Al.O_6.K_2.$$

As a rule part of $OH^{1-}$ is replaced by $F^{1-}$. In biotite the group of $4Al^{3+}$ in the middle is replaced by $6Mg^{2+}$.

The structure of margarite is similar, but with further replacement of the silica of the muscovite by aluminium and the incorporation of Ca instead of K to make up the negative charge:—

$$Ca_2.O_6.Si_2Al_2.O_4(OH)_2.Al_4.O_4(OH)_2.Si_2Al_2.O_6.Ca_2.$$

In chlorite, mica-like layers having the structure:—

$$\{O_6.Si_3Al.O_4(OH)_2.Mg_6.O_4(OH)_2.Si_3Al.O_6\} =$$

alternate with brucite-like layers with the structure:—

$$\{(OH)_6.MgAl_2(OH)_6\}^{++},$$

the former being negative, the latter positive.

It is thus not difficult to see that such structures would on decomposition give rise to products of the kaolin type.

Minerals consisting of a three dimensional network of silicon and oxygen, *e.g.* feldspars, have quite a different structure, with no direct relationship to the kaolin structure, and it would be expected that on weathering a rearrangement of atoms in the structure would take place. As a result of the study of kaolin deposits Ross and Kerr (**11**) concluded that there is no evidence for the formation of

muscovite from feldspars, and that the "muscovite-like" mineral occurring in such deposits approximates to kaolinite but contains less water. On the other hand, Tamm (**13**) and Zemiatchensky (**15**) assert that a mineral resembling muscovite is an intermediate product in the weathering of feldspars. Zemiatchensky states that this product is optically and chemically akin to muscovite but contains more water. Unfortunately Zemiatchensky was unable to follow up the further decomposition of this intermediate product, since it is apparently very stable. No formation of kaolinite was observed.

Kerr (**8**) has given a good example of the formation of kaolinite from biotite. Apparently an isotropic brown gel-mineral is the first product. This then grades into a green gel-mineral phase, which in its turn passes into a pale green gel-mineral and finally changes to kaolinite. The progressive loss of colour and structure in the sequence of gel-minerals suggests the reduction and removal of iron.

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